

THE DETERMINATION OF SULFUR
IN IRON AND STEEL

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The Determination of Sulfur in Iron and Steel

With a Bibliography 1797-1921

BY

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PREFACE.

The determination of sulfur in iron and steel is one of those chemical control analyses which are fundamental to a surprisingly great amount of present-day engineering. The ores of iron are carefully analyzed for iron, phosphorus and sulfur before and after mining; the iron blast furnace is run with special reference to the silicon, sulfur and phosphorus in its product, and finally the transformation from iron to steel is minutely controlled with reference to the final content in carbon, manganese, phosphorus and sulfur. In foundry practice the five elements are closely regulated because of their influence on final structures, the transformations in making malleable iron and the properties of the final shapes. The sulfur content of steel must be kept below narrow limits for working the metal and for superior physical properties in the finished stock.

Thousands of sulfur determinations are daily made with the same regularity as the firing of the furnaces; there is no indication but that chemical control as represented in this determination of sulfur is to become more general and more exacting. The cost per determination should become less even with increase in precision. Lack of suitable accuracy and agreement between analysts is already calling for exhaustive research; the actual condition may be partly judged from the figures presented in the bibliography; a special survey of current precision and checking by different methods would unquestionably disclose a state of analysis not at all flattering.

This study of the determination has been assembled, not in a desire to obviate or forestall original work, but, that whatever work is to be done may be accomplished more intelligently, more thoroughly, and with past attainments as the starting point for new ones. A considerable amount of work has been repeated to slight advantage because previous work was unknown and some of the best work lies practically hidden in the pages of old journals and foreign publications. Some of the material will be interesting to the works' analysts as well as to the chief chemists and to the research men.

The aim has been to include all numerical analytical data of importance contained in the articles referred to. Except for the completeness of the bibliography many copyrighted articles might be omitted with advantage. The bibliography contains articles directly relating to the subject; apparently the literature contains an equal number on the determination of sulfur in pyrites as well as many on sulfuric acid and barium sulfate which may be highly important but have slight relation to quantitative work involving the small amounts of either which come from the ferrous materials. A percentage error of two or three means a great deal in determining sulfur in pyrites but is of no significance whatever in determining sulfur in iron and steel.

Many of the references indicate that a mere opinion or a few results have no force and trivial value; while no work has yet been published which is comprehensive enough to give a distribution of results curve on even one sample.

In reviewing the history of the determination one is carried back to the beginnings of wet analytical chemistry. The chemist finds a peculiar pleasure in following the developments of the technique and the introduction of new ideas; colorimetric, volumetric and gravimetric methods are both early and recent. The more modern chemical theories and modes of ion precipitation and concentration measurement have not yet noticeably affected the character of the determination. Radical developments may be expected whenever we can more penetratingly measure the concentration of $S^{=}$ and $SO_4^{=}$ ions. The mere presentation of the case may supply the basis for more and better accomplishments.

LEHIGH UNIVERSITY,

May, 1922.

CONTENTS.

	PAGE
SULFIDS IN THE FERROUS MATERIALS	I
Sulfur Compounds and their Solubilities	2
Crystallization and Segregation	3
Sampling and Grinding	8
METHODS OF ANALYSIS	10
Liberating the Sulfur	12
Measuring the Sulfur	19
Outline of Methods	22
The Nitric Acid Method	22
Bamber's Method	25
The Chloric Acid Method ..	27
The Evolution Method	29
RESULTS OF ANALYSES	33
THE PRECISION OF RESULTS	46
Constant Errors	49
Chance Errors	50
Distribution of Results	50
Bibliography	53

LIST OF ILLUSTRATIONS.

FIG.	PAGE
1. Influence of Ingot Size on Enrichment (Howe)	4
2. Iron Sulfid Network	5
3. Good and Bad Spots in Steel	6
4. Sulfur Print of Iron Ingot	6
5. Sulfur Print of Rail Section	7
6. The Author's Evolution Flask	17
7. Battery of Three Evolution Flasks	30

SULFIDS IN THE FERROUS MATERIALS.

The determination of sulfur in iron and steel, like so many other analyses of commercial products, is liable to widely fluctuating results because of improperly sampled stock, because of segregation in the sample selected, and because of many constant and fortuitous errors inherent in determining a minute constituent easily diminished or augmented. It thus often happens that the determination of sulfur is far from completed by weighing out a 5-gram portion and recovering its sulfur in some accurately measured amount of cadmium sulfid or barium sulfate. A check determination may not agree with the first result, a duplicate sample may differ from the first results while if another analyst tries the same or another method the uncertainty of the results may only be increased. In short, the sulfur determination may be expected to check itself better than one part in ten only by using selected material, by using finely ground sample and adhering to the most minute detail of duplication with the different lots run. The analysis does not at all resemble similar determinations made on pure salts, on ground and mixed powders, or on portions selected from homogeneous solutions.

The analyst who may be called upon to make sulfur determinations and check his own and the work of others would often refuse in disgust if he could only see the actual condition of the sample. The chips of metal may look uniform and may have come from the same hole in a piece of metal yet the sulfur distribution be so unequal as to preclude any probability of satisfactory results. Routine plant analyses for comparative and crude control results often demand slight attention but real control work, standardization, testing, scientific and court work, and analyses requiring precision, all exact personal attention in the sampling and preparation of the sample. The nature of the original massive stock is a matter of the utmost importance. Another vital and fundamental condition of accurate sampling is that no division of the material shall be based on any inequality such as size of particles; a sample selected with the use of a sieve may be expected to have decidedly different sulfur content in the two portions.

Sampling and analysis are two mutually dependent and very closely related operations; poor work in either wastes splendid effort on the other. Sampling which may be perfect for some components may be intolerable for other components; the true iron in two 5-gram lots might vary from 99.93 to 99.97 per cent. and be more accurate than necessary but if the slight variation from 0.07 to 0.03 per cent. is a matter of the difference in sulfur content the sampling is very bad and precise analytical work discredited.

Sulfur Compounds and Their Solubilities.

There are several forms in which sulfur is known to exist in ferrous stock. The most common compounds are ferrous sulfid (FeS), manganese sulfid (MnS), and the double iron-manganese sulfid (Fe, MnS). It is not to be supposed that the sulfids separate chemically pure or that they are wholly insoluble even in the cold metal. Tammann¹ states that an excess of iron always separates with the sulfids and that, conversely, the sulfids are slightly soluble in iron.

In 1901 Blair and Shimer discovered a sulfid containing titanium, carbon and iron which is insoluble in dilute hydrochloric, but dissolves in nitric acid. The complex sulfid occurs as hexagonal scales and has the following composition: Ti, 62.82 per cent.; S, 22.64 per cent.; C, 9.82 per cent., and Fe, 1.82 per cent. The compound is met with in certain titaniferous irons; Blair and Shimer do not state the solubility of the sulfid in concentrated hot hydrochloric acid.

Other investigators have tried to establish more sulfur compounds, especially some containing carbon, but at this writing no adequate confirmation of such compounds is at hand.

Researches made on the solubilities of ferrous and manganese sulfids indicate that they are soluble in limited proportions above the melting point of the metal; the sulfids are also somewhat soluble as solid solution in gamma-ferrite or austenite, but separate as the nearly pure sulfids when gamma-transforms to beta- and alpha-ferrite or whenever austenite cools below its temperature of

¹ Tammann, "Lehrbuch der Metallographie."

stable equilibrium. The final transformation or separation of solid sulfid from ferrite occurs at as low a temperature as 130°C .¹ The sulfids should accordingly be visible at room temperatures in properly prepared specimens as separated and discrete masses, globules, layers and films.² The influence of carbon, silicon and manganese introduces new complications not yet fully solved by systematic research. Manganese acts as a desulfurizer by displacing iron and floating to the surface of a melt as manganese sulfid; the flotation of the sulfid is apparently at variance with its supposed solubility in the melt.

Crystallization and Segregation.

The solidification of the ferrous materials which necessarily takes place during the manufacture of practically all iron and steel is far from a simple congealing of the mass, it is a complicated differential crystallization involving crystal growth, the extrusion of solid, liquid and gaseous impurities as well as arranging their distribution in anything but the uniform manner previously found in the molten metal. The gradual spread of the solidification from the exterior to the center of the mass involves concentrations of impurities toward the last parts solidifying. Local pocketings occur as well as the anchoring of particles attached to gas bubbles and the extrusion of compounds during the allotropic transformations. The several inequalities are more or less permanently preserved through the mechanical and heat treatments of the material and appear in the finished shapes.

The distribution of sulfur in any object can be demonstrated by chemical analysis, by sulfur prints, and by the microscope either visually or photographically. Chemical analysis discloses the conditions possibly somewhat softened by the integrating effect of a 5-gram sample, the sulfur print and the microscope localize the areas of high and low sulfur vividly enough but in a more qualitative manner. Several authors have presented the subject in admirable manner especially since Heyn and Bauer, in 1906, initiated the use of sulfur prints. The treatises by Bauer and

¹ Guertler, "Metallographie," I, I, p. 978.

² Osmond and Stead, "Microscopic Analysis of Metals."

Deiss,¹ Hatfield,² Sauveur³ and Edwards⁴ each present their author's experiences relating to the distribution of sulfur and are well illustrated. Dr. H. M. Howe, of Columbia University, has written elaborately over a period of some decades concerning the nature of ingots; in a short paper presented in 1909⁵ he gives figures to show the accentuation of segregation with increase in ingot size. Silicon and manganese are as solid solution in the more common ferrous constituents of iron and steel but carbon and sulfur separate in particular compounds and are prone to be depleted in certain zones and increased in others. Fig. 1 is from

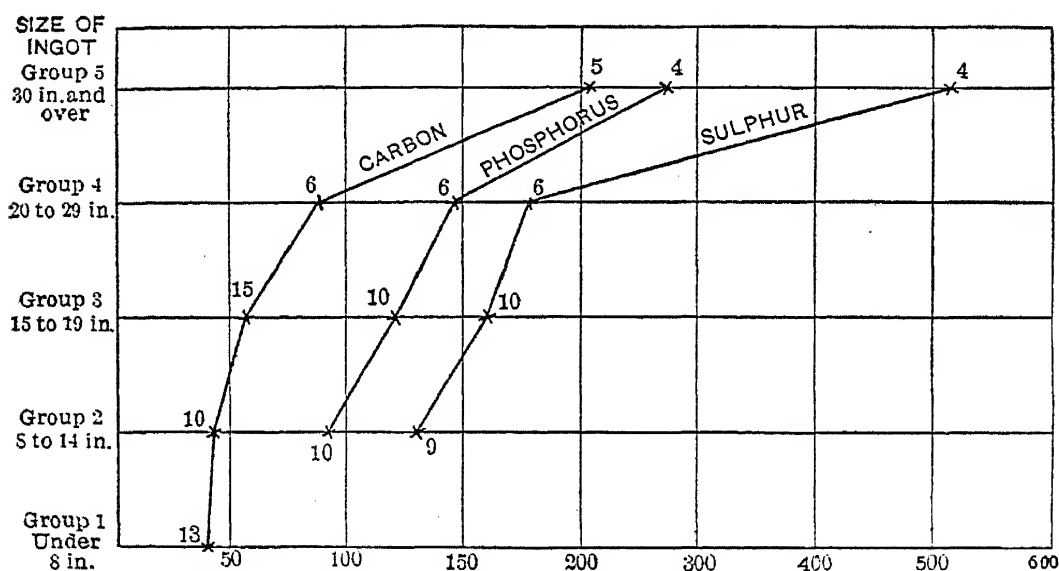


Fig. 1.—Influence of ingot-size on maximum enrichment in steel ingots.
Average "maximum enrichment" of each of the five groups, in per cent.

Dr. Howe's paper of 1909; it is plain that sulfur is the worst offender of the three segregating elements, it is worth observing that the variation of sulfur content is not a matter of a few per cent. but from 100 to 500 per cent.

Fig. 2 is a photograph from a special high sulfur steel ingot at a magnification of 430 diameters. The material contains 0.40 per cent. carbon, so the matrix is gray pearlite and white ferrite; 2.5

¹ Bauer and Deiss, "The Sampling and Chemical Analysis of Iron and Steel."

² W. H. Hatfield, "Cast Iron in the Light of Recent Research."

³ Albert Sauveur, "The Metallography and Heat Treatment of Iron and Steel."

⁴ C. A. Edwards, "The Physico-Chemical Properties of Steel."

⁵ Henry M. Howe, "The Influence of Ingot-Size on the Degree of Segregation in Steel Ingots." *Trans. Am. Inst. Min. Engrs.*, XL, p. 644 (1909).

per cent. sulfur was introduced to plainly demonstrate the occurrence of the ferrous sulfid which must accordingly be present to 6.5 per cent. of the total. The iron sulfid is seen as a network and as globules.

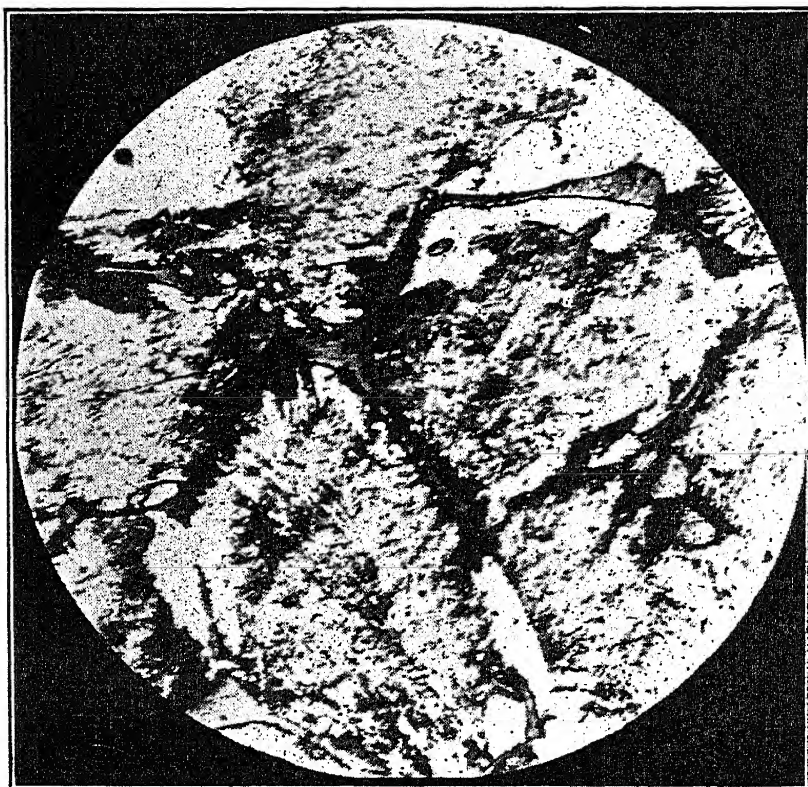


Fig. 2.—Iron sulfid network and globules in a 2.5 per cent. S steel ingot, x 430.
(Courtesy of Illinois Steel Co.)

Fig. 3 shows good and bad spots in a piece of low carbon steel; on the left is the normal ferrite with frequent pearlite spots along the grain boundaries; on the right is a large sulfid inclusion, the grain texture is gone and sulfid globules are numerous. The two spots were only one-half inch apart.

Fig. 4 is a sulfur print of a high sulfur cast iron ingot; a layer of sulfid extends entirely across the top of the ingot. It would obviously be a very difficult task to obtain an accurate sample of an object as non-uniform in sulfur content as indicated by Fig. 4.

Fig. 5 is a sulfur print of a section of a steel rail. The sulfur in the rail section is everywhere prominent, while in the rail-head are several very conspicuous sulfur spots. Drillings from the

Sampling and Grinding.

An adequate understanding of the distribution of sulfids in the ferrous materials should enable one to judge and direct how the sampling should be done in any particular case. For routine plant work where the material is repeatedly checked by analyses and otherwise promptly discloses any unusual deviations it may be sufficient to rely on one determination from a heat, or on one grab from a random pig, or on a grab drilling from a casting or test bar ingot. For more precise work the material must be sampled more thoroughly; many pigs must be drilled entirely through, or the entire cross-section of an ingot or shape must be milled across, or drillings from several places in an object or ingot may each constitute a sample and the sulfur limits become established. The sample should be ground and mixed for the best work. The use of lower and upper limits to define the sulfur content appeals more than an attempt to strike an exact average figure, since the latter, to embody any real precision, might demand an amount of work quite out of reason. If the head of a rail runs 0.045 per cent. sulfur and the flanges go 0.035 per cent. and the web has 0.065 per cent., the limits might be stated as 0.035 to 0.065 per cent. sulfur, or, by milling entirely across and mixing the ground chips an average figure of 0.050 per cent. might be found. The analyst has a very large responsibility in the sampling because he is the one who should best understand the entire situation and he should be the last one to court criticism for his very precise results on equally nondescript samples.

It might be interesting to inquire how fine a sample should be ground so that selections of 5-gram portions should not vary in sulfur content by more than 0.001 per cent. If a sample contains no particles whose sulfur content amounts to more than 0.001 per cent. on a 5-gram batch, and the sample is well mixed, then it makes no difference whether any one particle goes to the sample or reject and repeated selections should check each other to this limit. If single particles should contain enough sulfur to amount to 0.003 per cent. or 0.005 per cent. on a 5-gram portion, then some suppose that the theory of averages assures that other par-

ticles with lower sulfur content might balance and the average come exactly true; however, distribution curves demonstrate that such particles cannot be expected to exactly balance and the probable result will be about a certain amount one side or the other of the true average, depending on the quantities involved.

In a 5-gram sample of metal it requires about 0.00005 gram of sulfur or 0.00014 gram of iron or manganese sulfids to influence the result by 0.001 per cent. This amount of either sulfid is approximately represented by a cube of the material 0.3 mm. on a side; such a particle will barely pass the openings in a 50-mesh screen. To allow of some margin of safety the material should be fine enough to pass an 80-mesh screen, or finer; the entire sample should be thoroughly mixed before making any selections.

Now it is a very difficult operation to grind iron or steel as fine as 80-mesh; it is likewise probable that in attempting to grind so fine the heat of abrasion would oxidize more or less of the sulfur and a portion be lost. This conception of fine grinding is another argument for expressing results as within limits instead of attempting to state an exact figure for the sulfur content of any given object or material.

Probably the present best compromise for sampling any given object, be it a finished shape or a test ingot, is to mill entirely across a section which shall represent both the weight of the object and the locus of segregation; the millings should be as fine as possible, they are then ground, preferably in a coffee mill type of machine which has hardened surfaces, and finally mixed by rolling or shaking through a small riffle. Pig and cast irons may separate graphite and not become a pleasing product but it is doubtless the best that can be done. Nothing can be discarded nor is it permissible to sieve or make a screen sizing. For the preparation of standard samples it does not matter whether the product represents the original object or not; it is therefore an aid in getting the most uniform material possible to screen out both hard high-sulphur lumps and fine low-sulphur graphite or particles so fine that they are prone to segregate on handling and so impair the uniformity of the aggregate.

Methods of Analysis.

A perusal of the accompanying bibliography in the original allows one to classify the methods for sulfur determination according to the following scheme:

TABLE II.—METHODS OF DETERMINING SULFUR.

- I—Direct combustion in oxygen.
 - II—Volatilization as SCl_2 in chlorine at red heat.
 - III—Volatilization with H_2 and CO_2 at red heat as H_2S .
 - IV—Fusion of powdered sample with oxidizing alkaline salts; sintering of powder with MgO and NaOH .
 - V—Oxidizing both iron and sulfur with acid solution (or halogen); precipitation of sulfur direct or after various manipulations. The residue may be fused and its sulfur added to main portion.
 - A*—Bromine.
 - B*—Concentrated HNO_3 .
 - C*— KClO_3 and HCl .
 - D*—Aqua regia.
 - E*—Bromine and HCl .
 - F*— HNO_3 and KClO_3 and KBr .
 - G*—Chloric acid.
 - VI—Nitric acid solution and fusion of the evaporated mass.
 - VII—Solution of iron leaving sulfur and sulfides ready to filter off and oxidize by acids or fusion.
 - A*—Ferric chloride solution.
 - B*—Copper-alkali (Na , K , or NH_4)-chloride solution.
 - VIII—Sulfur evolved as H_2S with H_2SO_4 , or HCl , or both.
 - A*— H_2S oxidized to H_2SO_4 direct or after precipitation of a metal, weighing as BaSO_4 . Oxidation by:
 - 1—Bromine.
 - 2—Chlorine.
 - 3—Permanganate.
 - 4—Hydrogen peroxide.
 - 5—Sodium peroxide.
 - 6—Lead peroxide.
 - 7—Hydrogen flame and permanganate.
 - B*— H_2S determined volumetrically.
 - 1—Iodine titer directly.
 - 2—Iodine in excess and back with thiosulfate.
 - 3—Iodine liberated by KMnO_4 , back with thiosulfate.
 - 4—Direct titer with KMnO_4 .
- (Absorbents for these 4 are NaOH , KOH , salts of Pb , Cd and Zn)*

TABLE II.—METHODS OF DETERMINING SULFUR.—(*Continued*)

- 5— FeCl_3 is reduced to FeCl_2 and run back with $\text{K}_2\text{Cr}_2\text{O}_7$.
- 6— ZnS reduces Fe''' to Fe'' and back with KMnO_4 .
- 7—Absorb in NaOH and titrate with $\text{Pb}(\text{NO}_3)_2$.
- 8—Absorb in standard arsenite and back with iodine.
- 9—Absorb in AgNO_3 to AgS and KSCN titer.
- C— H_2S determined gravimetrically, weigh as CuO , Ag_2S , Ag , As_2O_3 or BaSO_4 .
- D—Colorimetric determination of H_2S .
 - 1—Use a Pb salt.
 - 2— Cd salt gives CdS .
 - 3—Absorb in As_2O_3 solution.
 - 4—Formation of methylene blue.
 - 5—Gives color to metal foil.
- E— H_2S precipitates PbS , to be read in graduated tube after whirling.

Concerning these methods of analysis a few explanatory remarks will indicate their relative importance and certain condition of use.

Method I has been abandoned, after trial, except for particular ferro-alloys.

Method II is justly dismissed without comment.

Method III has some figures to substantiate it, but has too many inherent difficulties.

Method IV has been supported by considerable evidence of accuracy and by several workers. The material is best very finely powdered, a serious objection. Manipulation may also be objected to. Extremely slight practical use apparently attaches to the method.

Method V is widely used in one or another form, especially for more precise work. Nitric acid used as solvent must be replaced by hydrochloric and the silica is best rendered insoluble by baking. The ferric chloride may be separated by ether or the iron may be precipitated with ammonia and either the sulphuric acid washed out of the hydroxide or the hydroxide dissolved out of the already precipitated barium sulphate. Ferric iron may be reduced to ferrous by a variety of reagents or the same prevented from entering the barium sulphate precipitate by using organic

substances to form complex ions unaffected by the precipitation. Residues remaining after the acid treatment of the original sample may get special attention and the sulfur recovered added to the main portion.

This method has been abundantly disparaged and can, of course, be proven inadequate by uncritical operators. On the other hand, the method has been substantiated by abundance of the best work and nothing less than fresh evidence can shake it. The precipitation of the barium sulfate in the ferric chloride solution has been checked as accurate by workers of six nations. A table covering this point is offered in this paper as bearing directly and unequivocally on this point.

Method VI is generally considered an excellent control method.

Method VII is both old and new and theoretically excellent; the slowness of solution is always against it.

Method VIII has received by far the most attention from earliest to latest times, as the history of sulphur determination ranges. Samples may be annealed before dissolving, without or with admixed reagents. The evolution may be affected by acid alone or in the presence of hydrogen or carbon dioxide, or both. The gases may be passed through a red hot tube. The residue may be oxidized wet or by fusion or treated with hydrogen and hydrochloric acid at a red heat, any recovery being added to the main portion. The cumulative evidence is that quick evolution with concentrated hydrochloric acid gives a close approximation if not the exact sulfur content. Only in unusual cases will sulfur persist in the residue.

Liberating the Sulfur.

The first necessity in any method for determining sulfur is to not only absolutely decompose the matrix but simultaneously get the sulfur separated and into the medium which shall hold it for further separation or recovery. Some types of methods have been found good and some highly unsatisfactory.

Direct combustion in an excess of oxygen, similar to the method for determining carbon, liberates part of the sulfur which can then be collected. Direct combustion in oxygen burns the sulfur

in the presence of a relatively enormous amount of basic oxide, and, although the temperature is above the theoretical decomposition range of ferric sulfate there is every reason to expect that basic sulfates are highly soluble in the first molten and then frozen ferric oxide and would be permanently retained. The impossibility of freeing all the sulfur under the conditions has been thoroughly testified to by several workers. The case is, in fact, quite different from the case of carbon which once changed to a gaseous compound has not the slightest tendency to linger or dissolve in the oxide. More recently it has been proposed to use direct combustion in combination with other bases for the decomposition of resistant alloys; in this case the entire residue is treated to recover the sulfur.

There is no doubt but that the ferrous matrix can be adequately decomposed and the sulfur volatilized by treating the sample with chlorine at a red heat; the disagreeable nature of chlorine and the bother of controlling the volatile ferric chlorid precludes the further discussion of the reagent; other methods far less difficult solve the problem for all practical purposes.

It has been proposed to volatilize the sulfur with hydrogen and sweep out the hydrogen sulfid with or without carbon dioxide; the matrix is in no way affected except to lose its sulfur and some oxygen. This treatment is in direct conflict with the principle that the matrix shall be decomposed; like several other similar propositions, notably Ledebur's method for oxygen, there is no assurance of liberating the element desired.

Not infrequently it is proposed to fuse, sinter or frit the finely powdered metal with alkaline salts from which aggregate the sulfur is leached as sulfate leaving the insoluble ferric oxide behind. The defects of this type of treatment will be discussed under Bamber's method; it suffices here to state that all such methods would be open to far more consideration were it only possible to powder the sample. All sponsors for the type of analysis insist that the sample be finely powdered, an operation of much greater necessity in sampling than analysis and one performable on only a few special materials.

Next to the method evolving sulfur as hydrogen sulfid the most common attack on ferrous matrix is by means of a powerfully oxidizing acid such as nitric; the reagent should dissolve the iron to an easily soluble ferric salt, the sulfur should be oxidized completely to sulfuric acid. The reagents proposed consist of—

1. Bromine in H_2O .
2. Concentrated HNO_3 .
3. $KClO_3$ and HCl .
4. Aqua regia.
5. Bromine in HCl .
6. HNO_3 and $KClO_3$ and KBr .
7. $HClO_3$ and HCl .

Obviously the system is to attack with halogen, nitric or chloric acid and leave the iron as bromide, chloride or nitrate. All these reagents attack successfully and the choice is more a matter of speed, thoroughness and convenience. Bromine reacts slowly and costs excessively. Concentrated nitric acid is usually used and is assumed as the reagent when the "wet oxidation method" is mentioned. Concentrated nitric attacks different materials in the most diverse manners: impure steels are hardly restrainable within the beaker, especially if finely divided; pure irons and resistant alloys dissolve slowly and can be put in solution within reasonable time only by adding small amounts of hydrochloric acid.

Sulfur may easily escape in the copious fumes if the nitric acid solution is done hastily; this fact has often been published and can be demonstrated at will with a series of lots, each dissolving at a different rate. It is, therefore, essential for accurate or concordant results when using nitric acid to dissolve with moderation and never omit using a cover glass. Further precautions, such as a long upright tube, have been proposed but are not necessary.

Chloric acid was proposed by the author and has certain advantages not granted any other reagent. A sample of iron or steel if fine and attacked with rather concentrated chloric acid dissolves very quickly and with slight gas evolution. It is advantageous to have some hydrochloric acid present to hold the ferric

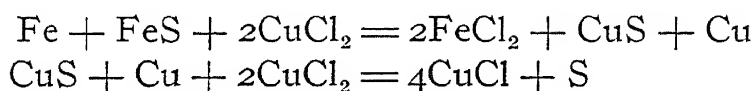
oxide in solution. Unfortunately chloric acid is expensive and usually contains sulfuric acid.

The insoluble titanium-carbon-iron-sulfur compound has been mentioned, other insoluble compounds may exist and there is also the possibility of a residue remaining which may hold sulfur especially with highly graphitic stock; it is frequently proposed to filter off any insoluble residue and make the recovery of the sulfur certain by a fusion with oxidizing salts such as sodium carbonate and nitrate. Additional treatment of this sort is doubly disadvantageous; it delays an already tedious analysis and it introduces new elements of error in each fresh manipulation.

Bamber's method is a combined acid and fusion method; the metal is broken up with nitric acid and then enough sodium carbonate is added to make alkaline and the entire mass evaporated and fused in platinum. The method demands the deliberate attack by nitric acid, the neutralization and evaporation spatters badly as does also the fusion; for efficient use of time the evaporation is best done in a steam vacuum desiccator with a current of air which has passed a cotton filter, the fusion is likewise best done in an electric muffle. The long evaporation, the several handlings and transfers, the filtering and washing, the use of so many reagents and the many hours which elapse between weighing out of the sample and final weighing up of the barium sulfate all offer so many chances for dust and impurities in reagents to augment the original few milligrams of sulfur that the author has found the method no more reliable than the simple nitric acid oxidation method. It is a case of precision overreaching itself to err on the positive side. Blanks aim to correct constant errors such as impurities in reagents, they fail before the chance errors so numerous involved in Bamber's method.

There is a method for dissolving away the ferrous matrix and leaving the sulfur insoluble as sulfid to be filtered off and oxidized to sulfuric acid; the reagents for this purpose are ferric chlorid and copper chlorid as well as the double chlorid of copper and either sodium-, potassium- or ammonium-chlorid. Berzelius was using CuCl_2 as early as 1840 for the carbon determination and

Gintl proposed the use of ferric chlorid in 1868; in 1871 Meineke found that the double copper-sodium chlorid dissolved the metal much more quickly. Although the method is rather slow in dissolving the iron there is no gas evolution and all the sulfur is unquestionably left behind. Dr. Adolf Classen in his "Ausgewählte Methoden Analytische Chemie," gives the following reactions to account for the sulfur remaining insoluble:



Whether it is necessary, or not, to consider the iron and manganese sulfids quickly transformed in the slightly acid solution to cupric sulfid and sulfur all conditions tend to hold the sulfur insoluble. As a working method the necessity for long standing or mechanical stirring, the risk of introducing sulfates with the salts, the additional filtration and acid treatment or fusion of the residue all result in placing the method outside those available for rapid or commercial work, but useful for scientific or standardization purposes.

The final method for decomposing the matrix and liberating the sulfur may be called the "evolution method;" either sulfuric or hydrochloric acid is used to both ionize the metal and liberate the sulfur as hydrogen sulfid which is swept away to be measured colorimetrically, volumetrically, gravimetrically, or oxidized to sulfuric acid and weighed as barium sulfate. Dilute and concentrated hydrochloric acid, dilute sulfuric, and mixtures of the two dilute acids have been used. Concentrated acid was used early in the history of sulfur determination but the more convenient manipulation with dilute acid has been in far more general favor and is yet probably the most common reagent for decomposing the matrix and liberating the sulfur. It has been many times published in the literature and can be demonstrated on almost any sample that dilute acid does not give the full amount of sulfur nor any constant or approximate percentage of the total sulfur; that dilute acid should be used at all may be laid to the urgency of cheap and approximate analyses. When concentrated acid is used rubber stoppers must be discarded and unless a condenser is used an un-

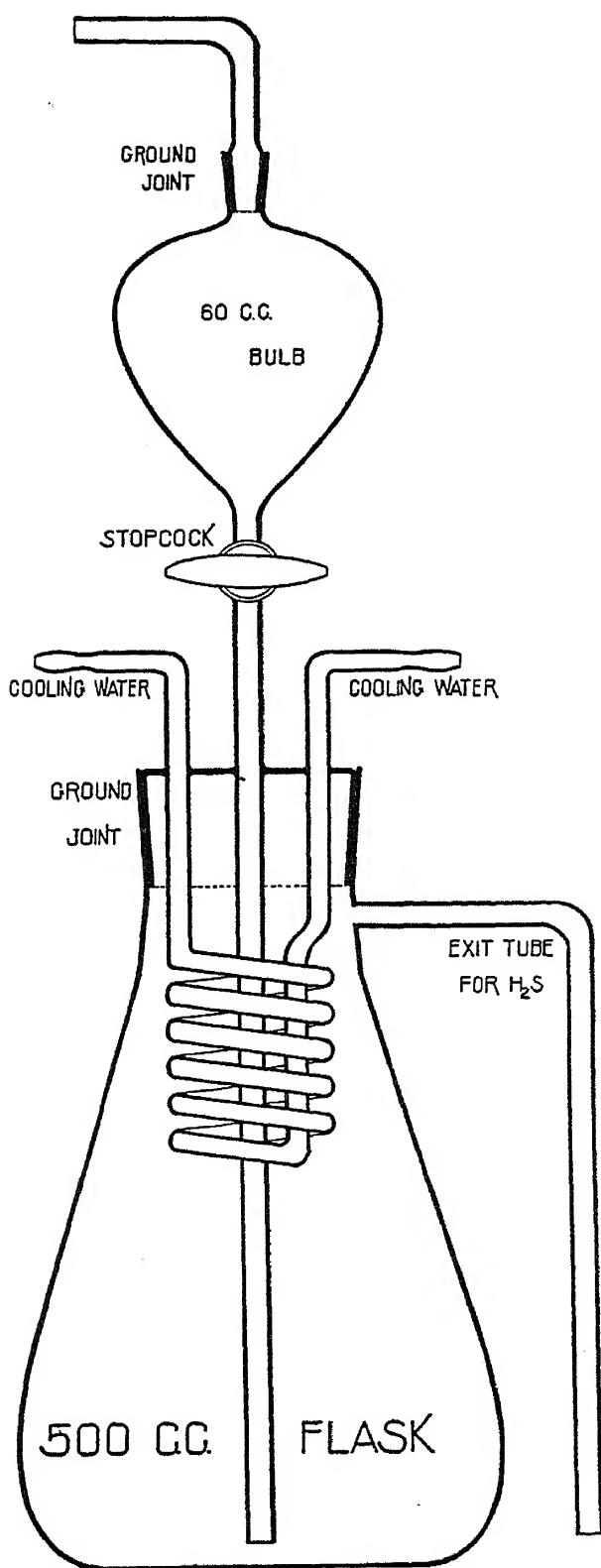


Fig. 6.—Diagram of the author's sulfur evolution flask.

due amount of acid distills over into the reagent absorbing the hydrogen sulfid.

Many designs for apparatus suitable to use concentrated hydrochloric acid have been published; their essential features are glass joints and a condenser in immediate proximity to the dissolving flask. Mention of apparatus will be found abundantly in the bibliography; after considering all these designs the author thought to make one yet more self-contained and handy. The author's design is seen in Fig. 6; because of the World War the first units were necessarily made in Japan; at the present time they are made¹ equally elegant and at reasonable cost in the United States. The design has proven easy of manipulation, rugged, and efficient in maintaining the concentration of the acid. With a battery of three units one operator can maintain a speed of nine determinations an hour and weigh out his own samples and titrate the results. The internal condenser conserves the acid strength so that at the end of an analysis the solution is stronger than at the start when 1 to 1 hydrochloric acid is used.

The concentrated acid not only effects more complete and speedy solution but the formation of methyl sulfid is probably wholly prevented. Since the decomposition of the sample and the liberation of the sulfur as hydrogen sulfid is one of the absolutely essential steps in the evolution method it might be supposed that all authorities would adhere to the use of concentrated acid as has since 1892 so often been proven necessary; the latest editions of Treadwell-Hall, Blair, and Scott recommended dilute acid while Lord and Demorest as well as White use concentrated acid with rubber stoppers; directions as given by Fay and the Bureau of Standards specify concentrated acid in all-glass apparatus.

Before the excellence of concentrated acid had been fully demonstrated the use of a red hot tube to decompose methyl sulfid as well as annealing of the sample had both come into certain vogue; both of these treatments increased the sulfur yield when using dilute acid but are now little heard of since the efficacy of concentrated acid has become recognized.

¹ They may be obtained of Schaar & Co., Chicago.

Measuring the Sulfur.

After the sulfur is once wholly liberated and changed to some compound for final color matching, volume measurement or weighing, the greater part of the difficulties are over.

The solubility of barium sulfate in the ferric chlorid solution is a small percentage error more or less compensated for by the addition of iron oxid, chlorine and silica. The author mixed composite residues of barium sulfate from Bamber's method, from the nitric acid method and from the chloric acid method and analyzed them for chlorine, ferric oxide and silica with the following results:

TABLE III.—ANALYSES OF BARIUM SULFATE FROM DETERMINATIONS.

	Chlorine	Ferric oxide	Silica	Total
Bamber's method	0.14	0.35	0.81	1.30
Nitric acid' method.....	0.21	0.79	0.49	1.49
Chloric acid method.....	0.11	1.64	1.23	2.98

The solubility of barium sulfate in ferric chlorid solution which is more or less acid with hydrochloric acid has long been a source of anxiety to analysts; a glance at the numerous recovery figures which are given in the bibliography indicates no appreciable loss, on the other hand, by looking for more sulfur in the filtrate the small additional amount usually found leads to the conclusion that it escaped precipitation and recovery in the first amount. It must be remembered that the dust, visible or invisible, which always floats in the usual commercial or analytical laboratory is rich in sulfates; when we add to this fact the traces of sulfates in reagents and on apparatus it need not be otherwise than expected that a more or less prolonged search for sulfate will be rewarded.

A series of twenty-eight direct tests was run to establish any appreciable increase of solubility of barium sulfate with increase of acidity. A measured amount of sodium sulfate was used as the source of the sulfion and by the addition of ferric chlorid solution the conditions of an actual analysis were approached.

The ferric chlorid solution was made by dissolving 560 grams of the pure solid salt in 2 liters of water, filtering and using 50 cc. in each case.

The sodium sulfate solution was made by dissolving 1.220 grams of the fused salt in 1 liter of water: 10 cc. were taken in each instance with a pipette delivering 9.996 cc., temperature corrected. All determinations were made at the same time with a volume of

TABLE IV.—DETERMINATIONS TO SHOW THE INFLUENCE OF HYDROCHLORIC ACID ON THE SOLUBILITY OF BARIUM SULFATE IN FERRIC CHLORIDE SOLUTION.

No.	FeCl ₃ Grams	Na ₂ SO ₄ Grams	HCl (1.19) Cc.	Weight BaSO ₄ Gram.
1	None	None	0.02	No ppt.
2	None	None	0.02	No ppt.
3	None	0.0122	0.02	0.0205
4	None	0.0122	0.02	0.0204
5	14	None	1.00	0.0001
6	14	None	1.00	0.0004
7	14	0.0122	0.20	Fe pptd.
8	14	0.0122	0.40	Fe pptd.
9	14	0.0122	0.60	Fe pptd.
10	14	0.0122	0.80	Fe pptd.
11	14	0.0122	1.00	0.0221 (red)
12	14	0.0122	1.20	0.0206 (red)
13	14	0.0122	1.40	0.0207 (pink)
14	14	0.0122	1.60	0.0204 (gray)
15	14	0.0122	1.80	0.0204
16	14	0.0122	2.00	0.0210
17	14	0.0122	2.20	0.0200
18	14	0.0122	2.50	0.0205
19	14	0.0122	2.80	0.0209
20	14	0.0122	3.10	0.0203
21	14	0.0122	3.50	0.0204
22	14	0.0122	4.00	0.0210
23	14	0.0122	4.50	0.0207
24	14	0.0122	5.00	0.0209
25	14	0.0122	5.50	0.0203
26	14	0.0122	6.00	0.0207
27	14	0.0122	6.50	0.0208
28	14	0.0122	7.00	0.0207
Average of last 17.....				0.0206
Average deviation				0.0002

120 cc.; precipitations were made hot; solutions stood at the boiling point for an hour, then over night before filtering. Precipitates were washed three times with hot dilute hydrochloric

acid (10 cc. 1.19 acid in 750 cc. water) and ten times with hot water.

The barium sulfate equivalent of 0.0122 gram Na_2SO_4 is 0.0200 gram BaSO_4 .

The results demonstrate that within the limits of the experiments the solubility of barium sulfate is not appreciably increased by increase of acidity, a conclusion in harmony with the theory of common ion effect. The same line of argument holds in regard to the purification of the few milligrams of barium sulfate; the best method of purifying a precipitate rich in iron is to repeat the analysis and put more hydrochloric acid in the solution, in fact this is about the only way to assure any precision; a fusion with carbonate involving the attendant manipulations and contact with reagents nullifies all good intentions and gives a final result no more accurate than a good guess. This is no reflection on the fact that scientific men might take such a precipitate and purify it and get a precision result; the trouble would cost many times the worth the entire sulfur determination; a works analysis is valued at only a few cents, even a custom analysis at a dollar or less.

As with barium sulfate so with most of the other end products which are measured as a means of determining the sulfur present. An end point involving the iodine-thiosulfate reaction is nominally precise to one part in a hundred or better; the several products of the solution in acid somewhat confuse the end point but at that it is probably far superior to the precision usually attained in the solution and production of the hydrogen sulfid. Sulfur results by different analysts and by different methods often vary by 20, 50 or 75 per cent.; compared with these huge variations the few per cents. by which barium sulfate or iodine end measurements deviate fade to insignificance.

Besides the barium sulfate and iodine titrations certain other end products are measured to gage the original amount of sulfur, some should be as accurate as these first two, some are not susceptible of much precision. A permanganate, dichromate or sulfocyanate titration should be accurate enough; colorimetric esti-

mations are difficult to read with much precision expressed in parts of the whole, as is also the case with measuring precipitates after whirling in a centrifuge. If the sampling is not expected to indicate the sulfur content any better than one part in five, as is often the case, then a colorimetric or measured precipitate is good enough. Obviously precision to one part in a hundred is wasted in an analysis if the sampling is accurate to only one part in five; gravimetric work would be inefficient for approximate results and one would use a rapid volumetric, colorimetric or volume of precipitate measure.

Outline of Methods.

THE NITRIC ACID METHOD.

The sample is mixed and 5 grams weighed out into a 250 cc. beaker and the cover-glass is placed. 30 cc. of concentrated (1.42 sp. gr.) nitric acid are poured in and the beaker gently warmed on a hot plate until action starts. Solution is controlled by cooling or warming until complete, when 20 cc. more of the same acid are added and the solution evaporated to dryness. Bake for 20 minutes at a temperature of about 200° C. and then set one side to cool. Add 30 cc. of concentrated hydrochloric acid and warm until residue is entirely free, then evaporate again to dryness and bake as before. Add 30 cc. of concentrated to the cooled beaker and warm to effect solution; evaporate cautiously to remove as much free acid as possible. Solution should get thick but not separate ferric oxide on cooling. Add 50 cc. water and 1 cc. concentrated hydrochloric acid; filter by suction and wash with hot water and 2 per cent. hydrochloric acid alternately. Adjust solution to 100 cc. if not already so and bring to boiling point; add 10 cc. of 10 per cent. barium chlorid solution and allow beaker to remain barely at boiling point on hot plate for an hour; set aside over night. In morning decant liquor through 7 cm. close, low-ash filter paper; discard the filtrate if clear, then wash in the precipitate with a fine stream of 1 per cent. hot hydrochloric acid. Wash six or eight times with the dilute acid, using not over 30 cc.; ignite wet, cool in desiccator; weigh.

Notes on Nitric Acid Method.

If the sample is not fine enough to give many hundred particles for the 5-gram sample there can be no assurance that consistent results can be obtained (unless the material is of known homogeneity), likewise the mixing should be done immediately previous to weighing out.

One and two gram samples are sometimes specified; so small a weight both shows up too strongly inequalities in the material and supplies too little barium sulfate for precision measurement. Ten-gram samples are sometimes advocated; this quantity is excellent for consistency and weight of barium sulfate but in quantity of reagents and size of beakers gets into the distinctly selected class of analyses, good for important cases but too expensive for routine or custom work.

Some samples will be only slightly affected by the acid as it heats up, other samples may foam entirely out of the beaker; watchfulness and skill are required to get the samples into solution. A sample dissolving quickly with a strong blast of fumes from the beaker will give less sulfur than when dissolved gently, as should be insisted upon. For pure irons and resistant alloys drops of hydrochloric acid may be added; such samples may be especially explosive as the passivity is intermittently broken down.

A second addition of nitric acid is made to assure complete solution of an elemental sulfur which is frequently separated unoxidized from high sulfur irons; for material known to be low in sulfur, that is, less than 0.020 per cent., the addition is hardly necessary.

Most authors, as for instance the Bureau of Standards directions, state that sodium carbonate should be added at some time previous to the baking on the hot plate. The ordinary hot plate temperature is from 200° to 300° C. on its upper surface; the lowest decomposition temperature for ferric sulfate, in a current of air, is given by Hofman and Wanjukow¹ as 492° C. In the case of a few milligrams of ferric sulfate buried in five grams of ferric oxide in a covered beaker there can certainly be no cause

¹ *Trans. Am. Inst. Min. Engrs.*, Vol. XLIII, p. 523.

TABLE V.—PER CENT. OF SULPHUR IN A FIVE-GRAM SAMPLE FOR
WEIGHTS OF BARIUM SULPHATE.

BaSO ₄ Grams	S Per cent.	BaSO ₄ Grams	S Per cent.	BaSO ₄ Grams	S Per cent.
0.0001	0.000	0.0195-6-7-8	0.054	0.0391-2-3-4	0.108
0.0002-3-4-5	0.001	0.0199-0-1	0.055	0.0395-6-7-8	0.109
0.0006-7-8-9	0.002	0.0202-3-4-5	0.056	0.0399-0-1	0.110
0.0010-1-2	0.003	0.0206-7-8-9	0.057	0.0402-3-4-5	0.111
0.0013-4-5-6	0.004	0.0210-1-2	0.058	0.0406-7-8-9	0.112
0.0017-8-9	0.005	0.0213-4-5-6	0.059	0.0410-1-2	0.113
0.0020-1-2-3	0.006	0.0217-8-9	0.060	0.0413-4-5-6	0.114
0.0024-5-6-7	0.007	0.0220-1-2-3	0.061	0.0417-8-9	0.115
0.0028-9-0	0.008	0.0224-5-6-7	0.062	0.0420-1-2-3	0.116
0.0031-2-3-4	0.009	0.0228-9-0	0.063	0.0424-5-6-7	0.117
0.0035-6-7-8	0.010	0.0231-2-3-4	0.064	0.0428-9-0	0.118
0.0039-0-1	0.011	0.0235-6-7-8	0.065	0.0431-2-3-4	0.119
0.0042-3-4-5	0.012	0.0239-0-1	0.066	0.0435-6-7-8	0.120
0.0046-7-8-9	0.013	0.0242-3-4-5	0.067	0.0439-0-1	0.121
0.0050-1-2	0.014	0.0246-7-8-9	0.068	0.0442-3-4-5	0.122
0.0053-4-5-6	0.015	0.0250-1-2	0.069	0.0446-7-8-9	0.123
0.0057-8-9	0.016	0.0253-4-5-6	0.070	0.0450-1-2	0.124
0.0060-1-2-3	0.017	0.0257-8-9	0.071	0.0453-4-5-6	0.125
0.0064-5-6-7	0.018	0.0260-1-2-3	0.072	0.0457-8-9	0.126
0.0068-9-0	0.019	0.0264-5-6-7	0.073	0.0460-1-2-3	0.127
0.0071-2-3-4	0.020	0.0268-9-0	0.074	0.0464-5-6-7	0.128
0.0075-6-7-8	0.021	0.0271-2-3-4	0.075	0.0468-9-0	0.129
0.0079-0-1	0.022	0.0275-6-7-8	0.076	0.0471-2-3-4	0.130
0.0082-3-4-5	0.023	0.0279-0-1	0.077	0.0475-6-7-8	0.131
0.0086-7-8-9	0.024	0.0282-3-4-5	0.078	0.0479-0-1	0.132
0.0090-1-2	0.025	0.0286-7-8-9	0.079	0.0482-3-4-5	0.133
0.0093-4-5	0.026	0.0290-1-2	0.080	0.0486-7-8-9	0.134
0.0096-7-8-9	0.027	0.0293-4-5-6	0.081	0.0490-1-2	0.135
0.0100-1-2-3	0.028	0.0297-8-9	0.082	0.0493-4-5-6	0.136
0.0104-5-6-7	0.029	0.0300-1-2-3	0.083	0.0497-8-9	0.137
0.0108-9-0	0.030	0.0304-5-6-7	0.084	0.0500-1-2-3	0.138
0.0111-2-3-4	0.031	0.0308-9-0	0.085	0.0504-5-6-7	0.139
0.0115-6-7-8	0.032	0.0311-2-3-4	0.086	0.0508-9-0	0.140
0.0119-0-1	0.033	0.0315-6-7-8	0.087	0.0511-2-3-4	0.141
0.0122-3-4-5	0.034	0.0319-0-1	0.088	0.0515-6-7-8	0.142
0.0126-7-8-9	0.035	0.0322-3-4-5	0.089	0.0519-0-1	0.143
0.0130-1-2	0.036	0.0326-7-8-9	0.090	0.0522-3-4-5	0.144
0.0133-4-5-6	0.037	0.0330-1-2	0.091	0.0526-7-8-9	0.145
0.0137-8-9	0.038	0.0333-4-5-6	0.092	0.0530-1-2	0.146
0.0140-1-2-3	0.039	0.0337-8-9	0.093	0.0533-4-5-6	0.147
0.0144-5-6-7	0.040	0.0340-1-2-3	0.094	0.0537-8-9	0.148
0.0148-9-0	0.041	0.0344-5-6-7	0.095	0.0540-1-2-3	0.149
0.0151-2-3-4	0.042	0.0348-9-0-1	0.096	0.0544-5-6-7	0.150
0.0155-6-7-8	0.043	0.0352-3-4	0.097	0.0548-9-0	0.151
0.0159-0-1	0.044	0.0355-6-7-8	0.098	0.0551-2-3-4	0.152
0.0162-3-4-5	0.045	0.0359-0-1	0.099	0.0555-6-7-8	0.153
0.0166-7-8-9	0.046	0.0362-3-4-5	0.100	0.0559-0-1	0.154
0.0170-1-2	0.047	0.0366-7-8-9	0.101	0.0562-3-4-5	0.155
0.0173-4-5-6	0.048	0.0370-1-2	0.102	0.0566-7-8-9	0.156
0.0177-8-9	0.049	0.0373-4-5-6	0.103	0.0570-1-2	0.157
0.0180-1-2-3	0.050	0.0377-8-9	0.104	0.0573-4-5-6	0.158
0.0184-5-6-7	0.051	0.0380-1-2-3	0.105	0.0577-8-9	0.159
0.0188-9-0	0.052	0.0384-5-6-7	0.106	0.0580-1-2-3	0.160
0.0191-2-3-4	0.053	0.0388-9-0	0.107		

for alarm as to decomposition of the sulfate unless the temperature is above 400°C. , a temperature far too high for safe boiling or evaporations.

It is assumed the analyst is familiar with the folding and placing of filter papers as well as the technique of washing with small volumes of liquid; the washing of the barium sulfate precipitate, thoroughly and with a minimum of liquid, and without running through or creeping of the precipitate is relatively important with the small total amount of solid involved. Measures may be taken to grow still larger crystals of the sulfate but if the directions are followed there will be slight trouble.

A precipitate obviously contaminated with ferric oxide may be purified by treatment with hydrochloric acid or fusion, but the better practice is to repeat the determination.

All reagents used must be tested for sulfur; no significant amount should be obtained with the amount of reagent used in an analysis.

Blanks should be run simultaneously with the samples.

BAMBER'S METHOD.

5 grams of the well-mixed sample are weighed into a 250 cc. beaker and the cover-glass placed; 40 cc. of concentrated (1.42 sp. gr.) nitric acid are added and solution effected as in the nitric acid method. When red fumes are no longer evolved 10 grams of sodium carbonate are added and a little water to soften the mass. The entire mass is washed out into a platinum dish, the beaker is scrubbed out completely with a policeman and the rinsings added to the main portion in the dish. Several of the dishes may be placed beneath a large cover glass in a vacuum desiccator in which the pressure is reduced to 15 or 10 inches and the temperature is held at about 95°C. Air is admitted to the desiccator through a frequently renewed thick cotton filter maintaining the same reduced pressure. At the end of 8 or 9 hours when the contents of the dishes are fully dried they may be removed to a muffle already heated and held from 1 to 3 minutes at the temperature of 900°C. After cooling the contents are covered with water and allowed to stand until disintegrated, probably over

night. The softened mass is stirred with a little more water in the same dish and then transferred to an 11 cm. filter paper. The filtrate is received in a 300 cc. casserole. The platinum dish is well scrubbed out with 2 per cent. sodium carbonate solution and then the mass of oxide and filter is washed six times with the same solution. The casserole being covered with a glass, 20 cc. of concentrated hydrochloric acid are added with stirring and the casserole is set on a hot plate, preferably electric, and evaporated to dryness. When dry and baked for a half hour 10 cc. more hydrochloric acid are added and the evaporation and baking repeated. The cooled salt is moistened with 1 cc. concentrated hydrochloric acid and then dissolved in 75 cc. of water. The solution is filtered through a 9 cm. filter paper into a 150 cc. beaker; the casserole is thoroughly scrubbed out and the washings added to the filter after which the paper is washed six times with small additions of hot water. The volume of the filtrate is adjusted to 100 cc., thoroughly stirred, heated to boiling, 10 cc. of 10 per cent. barium chloride solution added, set to incipient boiling for an hour then to stand at room temperature over night. In the morning the barium sulfate precipitate is filtered, washed, ignited and weighed as described under the nitric acid method.

Notes on Bamber's Method.

The final precipitation of barium sulfate is made under very favorable circumstances, otherwise all the operations of Bamber's method may become sources of error.

The first solution of the iron must be made with the same precautions as in the nitric acid method. Sodium carbonate is much more liable to contain sulfates than either hydrochloric or nitric acids. Losses by spattering during the addition of the carbonate and through the drying and ignition stages must be carefully guarded against; a cover glass should be over the material at all stages. The long stages of evaporations and filtrations are periods for the accumulation of sulfur-bearing dust; every precaution must be taken; any neighboring work or operation in the same room liberating sulfur-containing gases might be fatal to a whole batch of the determinations; the floor must not be swept if

the work is under way. If it is attempted to wash the ferric oxide precipitate with hot water alone the oxide will inevitably run through in colloidal form. In the final sintering of the dried mass it should become red hot and thoroughly molten; it is not necessary to hold till a quiet fusion is obtained which will form much caustic and destroy the paper on filtering.

One or more blanks should go through simultaneously with the samples; they will help establish the final figures. Because of the long involved operation blanks also are subject to chance errors and thus differ from the usual blank which should record with precision some constant quantity.

THE CHLORIC ACID METHOD.

Weigh 5 grams of the well-mixed sample into a 400 cc. beaker and place the cover glass. Moisten the sample with water and disperse the grains over the bottom of the beaker. Add 40 cc. chloric acid, sp. gr. 1.20, and when sample is dissolved add just enough hydrofluoric acid to dissolve any separated silica, but no excess. Add 10 cc. concentrated hydrochloric acid and digest 2 or 3 minutes over a flame. Filter by suction through a 7 cm. paper; add 10 cc. concentrated hydrochloric acid to the filtrate and set on hot plate to evaporate to small volume. The filter paper containing the residue is placed on a thin bed of sodium peroxide and sodium carbonate in a silver or nickel crucible, more mixture is placed on top of the paper and the cover placed. The crucible is placed in a triangle and with the cover held down with the tongs a free flame is placed under the crucible. As a red heat is obtained the contents ignite with a poof after which the melt may be swirled in the flame until the reaction is complete; pour the fusion onto a cold metal plate. Dissolve the button and residue in crucible in a little water in a 250 cc. beaker; after rinsing out the crucible, filter through 7 cm. paper by suction and acidify the solution with hydrochloric acid, add filtrate to the main portion, which should now be syrupy. Adjust the solution to 100 cc., heat to boiling, add 10 cc. 10 per cent. barium chlorid solution, set to digest, hot, for an hour; let stand at room temperature over night. In the morning decant through a 7 cm. paper, trans-

fer the precipitate to paper with 2 per cent. hydrochloric acid solution, wash six times with the same solution, ignite, cool, and weigh.

Notes on the Chloric Acid Method.

Commercial chloric acid usually contains either sulfuric acid or barium; the sulfuric acid may be precipitated with barium chlorate crystals.

The sample is moistened and spread over the bottom of the beaker to avoid cementing the ferric oxid into a solid mass.

During the solution of the sample, which takes place in a minute or two, the solution may boil and slight explosions of chlorine dioxid displace the cover glass; the gas evolution is very moderate and solution wonderfully prompt.

The hydrofluoric acid is added to hold silica in solution; the amount added should correspond to the silica present and be as little as possible. Sodium fluosilicate which may form and crystallize out is rather insoluble; it appears in large almost transparent crystals which, if present, must be dissolved away from the white opaque barium sulfate with hot water.

While the residue is being fused and dissolved the main portion will evaporate to a syrupy consistency ready for the second portion.

Use as little of the sodium peroxid, sodium carbonate mixture as possible, only enough to burn the paper and fuse the residue. The fusion requires only a couple of minutes and the dissolving is also prompt. Elapsed time from weighing out sample to setting aside to digest with barium chloride added need not require more than 20 minutes.

If a silver crucible is used beware of melting out the bottom; remember that silver fuses at 960.5° C., a full red heat.

Blanks should be run with this as with any method.

Chloric acid is the quickest and most perfect dissolving reagent which the author has learned of; the disadvantages are the cost, the impurities, the dissolving of silica with hydrofluoric acid and the separation of sodium fluosilicate. The absence of strong gas evolution, the avoiding of evaporation to dryness, and the short

time required are all much to be desired. The chloric acid method holds promise of having its disadvantages overcome, something not to be expected of the nitric acid or Bamber's method.

THE EVOLUTION METHOD.

Weigh 5 grams of the well-mixed sample and cautiously brush into the flask so that no particles fall against the sides, 40 cc. of hydrochloric acid, sp. gr. 1.19, having been put in the bulb the stopper is adjusted tightly. The absorbent solution is prepared by putting 300 cc. of water in a 500 cc. beaker of the tall form; to this is added 20 cc. ammonia, sp. gr. 0.90, and 10 cc. of ammoniacal cadmium chlorid solution (300 grams CdCl_2 , 500 cc. ammonia, sp. gr. 0.90, and 500 cc. water). The exit tube is adjusted in the beaker and the cover glass placed as closely as may be. The cooling water is regulated.

Hydrogen from hydrochloric acid on zinc is passed through alkaline permanganate and a safety bottle and let in at the top of the apparatus to force the acid down on the metal, the burner below is lighted. At the end of 15 minutes the flame is removed, the exit tube is withdrawn and washed off into the beaker, the hydrogen is shut off, the stopper is loosened and the coil washed off into the flask after which the stopper is hung on the side support ready for the next determination. The flask is emptied and rinsed ready for the next run.

With the iodine solution in a burette at a known mark 10 cc. of starch solution is poured into the beaker, 50 cc. of concentrated hydrochloric acid is poured in and with stirring and titrating the upper layers first the iodine is run into a strong permanent blue, which should last two minutes, the color is then discharged with thiosulfate solution.

Blanks are run under identical conditions omitting the iron and the quantity of iodine required is subtracted from the total quantity used by the samples.

Notes on the Evolution Method.

The apparatus indicated in Fig. 7 may conveniently be used for the determination. There are no rubber connections, the acid strength is well conserved, the vapors are fairly well cleaned of

spray in passing the coils, foam will probably not rise higher than to touch the coils, no harm will result if the flask is left to boil an hour or more.

Cadmium sulfid has the most convenient rate of solubility in dilute acid of any of the common metals, in its release of the hydrogen sulfid it is more suited than a simple alkali or any other metal sulfid.

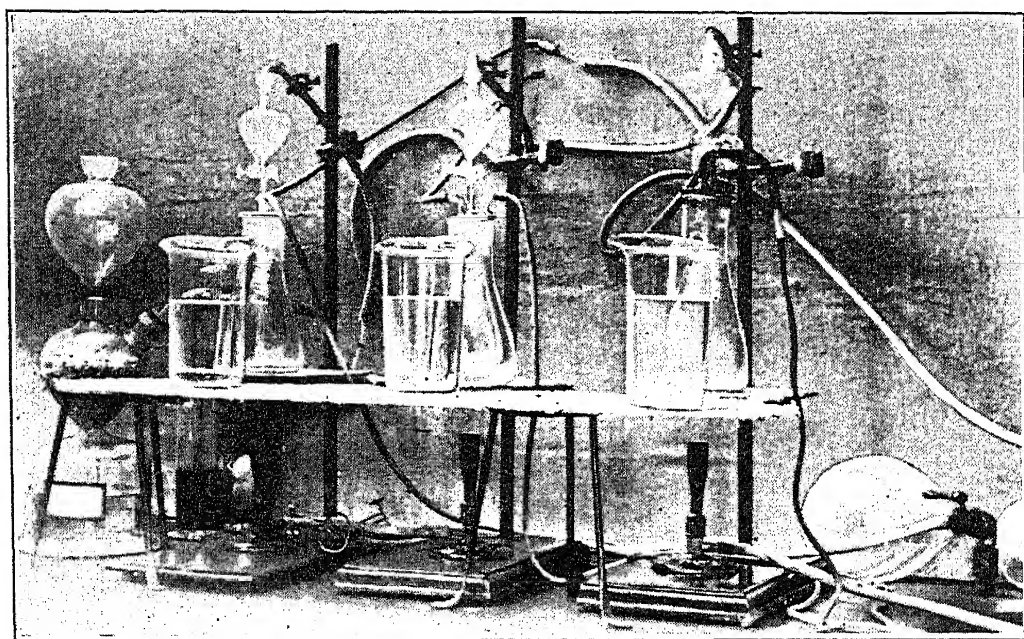


Fig. 7.—Battery of three of Author's units.

At first thought it might appear that some of the hydrogen sulfid liberated in the flask would escape from the loosely covered beaker; aside from the numerous assurances found in the literature actual trials at different rates of solution using Woulff bottles in series will convince one that the arrangement is wholly adequate.

Carbon dioxid may be used instead of hydrogen; ammonium bicarbonate is then apt to precipitate out in the beaker, on acidification large volumes of dioxid escape and if precipitated bicarbonate joins in the reaction the contents of the beaker may easily boil over.

The burner should be adjusted to hold the solution in gentle ebullition; the solution is thus maintained at maximum tempera-

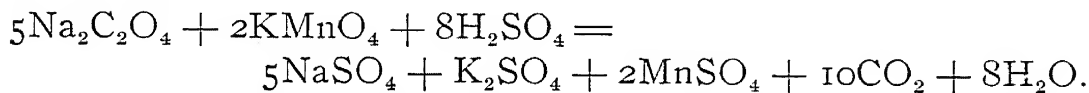
ture without undue loss of acid; the hydrogen is depended upon to sweep over the gases and prevent backward rush of absorbent when the strong hydrogen evolution from the sample shuts off.

The sample will probably dissolve in from 5 to 10 minutes if it is of ordinary materials. The amount of iron carried over into the beaker will vary greatly, depending on the character of the sample and the amount of heat applied; numerous measurements showed from a trace to 5 mg. carried over. If 0.01 mg. or less is carried over, the cadmium sulfid precipitate will be a clear lemon yellow; from 0.02 to 0.05 mg. colors the cadmium sulfid orange, while the sulfid is reddish with 1 mg. and over. The small amounts of ferrous salt carried over quickly oxidize to ferric hydroxid and are without influence on the subsequent iodine titration. A wisp of glass wool in the entrance to the exit tube will reduce the amount of iron passing over but does not change the results.

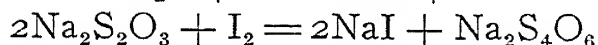
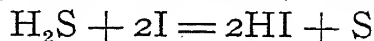
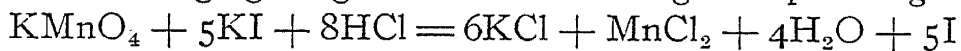
Filtering the cadmium sulfid before titrating merely raises the blank and does not change the net result.

As iodine is liberated from a solution of iodid by both ferric salts and hydrochloric acid the solution should not stand longer than necessary to wholly allow for decomposition of the cadmium sulfid; the author has found two minutes ample with the strength of acid specified; after discharge of the blue color the solution gradually turns blue from the liberated iodine.

The equations involved in the evolution method may be given as follows:



$(2 \times 158.03 = 316.06) / (5 \times 134.01 = 670.05) = 0.4717 =$
factor for changing weight of oxalate to weight of permanganate.



$\therefore 2\text{KMnO}_4$ is equivalent to 10I and to 5S.

$160.30/316.06 = 0.5072 = \text{S factor for KMnO}_4.$

$(\text{KMnO}_4 \text{ per } 1 \text{ cc./eq. cc. I}_2 \text{ sol.}) \times (\text{S eq. of KMnO}_4 \times 100)/5 = \text{the 5-gram sulfur factor.}$

TABLE VI.—STANDARDIZATION OF IODINE SOLUTION.

Permanganate and Oxalate.

$\text{Na}_2\text{C}_2\text{O}_4$	KMnO_4	To color	KMnO_4 per cc. (0.4717) (a)
0.3500	45.79	0.02	0.003607
0.3500	45.78	0.02	0.003608
0.3500	45.78	0.02	0.003608
0.3500	45.85	0.02	0.003602
0.3500	45.80	0.02	0.003606

Av. 0.003606

(a) Factor for changing weight of oxalate to weight of permanganate.

Permanganate and Thiosulfate.

KMnO_4	$\text{Na}_2\text{S}_2\text{O}_3$	Ratio
15.51	49.91	0.3108
15.00	48.22	0.3111
15.04	48.30	0.3114
15.01	48.30	0.3108
15.00	48.21	0.3111
15.02	48.35	0.3107
14.97	48.11	0.3112

Av. 0.3110

Iodine and Thiosulfate.

Iodine	$\text{Na}_2\text{S}_2\text{O}_3$	Ratio
49.82	47.10	1.058
49.80	47.21	1.055
49.62	47.08	1.054
49.91	47.22	1.057
49.76	47.11	1.056
49.80	47.22	1.055
49.78	47.19	1.055

Av. 1.056

1 cc. KMnO_4 is equivalent to 0.001829 g. S (factor = 0.5072).1 cc. KMnO_4 is equivalent to 3.395 cc. iodine solution.

1 cc. iodine solution on 5 g. sample in percentage equals 0.01077 per cent.

The standardization of the iodine solution is best accomplished through a thiosulfate and permanganate solution against standard sodium oxalate as supplied by the Bureau of Standards. The author prefers large bottles of all the reagents, in bulk from 20 to 50 liters, and made up some months in advance. If preserved in

the dark the solutions will alter so slowly that checking once a week is sufficient. As illustrating the precision and uniformity of the standardization work contrasted with the unequal distribution of sulfur in the metals, the above figures may be presented. It will be noticed that the variations between individual measurements are of the order of 1 part in 1,000 in the standardizations, while on the metal samples the sulfur content as measured by repetition under identical conditions will quite likely vary as much as 1 part in 5.

The evolution method has one important advantage over all the other methods; after the sample is inclosed in the flask and until the final precision measurement of the sulfur by the burette reading there is no exposure to a chance environment which may unwittingly either add or subtract sulfur from the lot of metal. In the results which will be found given for the samples investigated one sees that the evolution method frequently gives the highest figures; considering the splendid method available for standardizing the iodine solution and the absence of transfers and handlings as well as the impossibility of losing hydrogen sulfid the evolution deserves the most confidence for low-sulfur stock, high-sulfur material must receive special attention (due to the separation of elemental sulfur) by nearly all methods.

RESULTS OF ANALYSES.

A series of materials whose sulfur content varied from the lowest conveniently available to special high sulfur ingots served as the stock on which the following analyses were made. Results are reported on 29 samples. Many of the samples gave out before the work was finished and on the last five samples only the evolution method using concentrated acid was tried since they were Bureau of Standards samples.

The number of analyses is unquestionably only too small in practically every instance; 20 or 30 results by a single method is none too many for the adequate demonstration of the range of variation and most probable result. Unfortunately a really comprehensive and exhaustive study of this sort requires large resources in time, equipment, chemicals and financial support.

The analyses by the nitric acid method, the nitric acid-fusion (Bamber's) method and the chloric acid method were made as already outlined under their respective headings. The analyses by the dilute hydrochloric acid evolution method were made in an apparatus with rubber connections. If the 5 grams is to be annealed, it is wrapped in filter paper and placed in a small porcelain crucible and annealed for 15 minutes in a muffle at a red heat. All the samples analyzed by the concentrated hydrochloric acid method were run in the apparatus of the Fig. 6 type; a battery of three of these sets in which all of the recorded figures were obtained within a month and on the same permanganate, thiosulfate and iodine solutions is seen in Fig. 7. The blanks for the latter method varied from 0.20 to 0.40 cc. of the iodine solution.

The reagents used in the nitric acid oxidation method contained no appreciable sulfur in the quantity taken for single determinations and no blank has been deducted. The same applies to the results of Bamber's method. However, numerous blanks following through the course of Bamber's method gave an average sulfur recovery of 0.006 per cent. If this quantity is subtracted from the results the figures for the nitric acid method and Bamber's method check very closely indeed except in some four instances where they check almost exactly without the deduction.

The different lots of chloric acid contained slight amounts of sulfuric acid, even after precipitation with barium chlorate and blanks were run on each lot to provide the necessary deduction to be made on the total barium sulfate recovered.

The results by the evolution method using dilute hydrochloric acid were obtained in the apparatus with rubber connections and absorbing the hydrogen sulfid in sodium hydroxide solution; the indicated blanks were subtracted in all instances. It is evident that the annealed samples frequently agree fairly well with the direct samples and the oxidation methods on the low sulfur materials.

TABLE VII.—SUMMARY RESULTS OF ANALYSES.

Sample	Nitric acid method			Bamber's method			Chloric acid method			Evol. method, Dil. HCl—Direct			Evol. method, Dil. HCl—Anneal.			Evol. method, Conc. HCl		
	Lots	Av. % S	A. D.	Lots	Av. % S	A. D.	Lots	Av. % S	A. D.	Lots	Av. % S	A. D.	Lots	Av. % S	A. D.	Lots	Av. % S	A. D.
1	4	0.008	0.001	3	0.016	0.002	2	0.014	0.002	2	0.009	0.000	3	0.009	0.000	—	—	—
2	4	0.009	0.001	4	0.018	0.002	3	0.014	0.003	4	0.008	0.001	4	0.009	0.001	9	0.021	0.001
3	3	0.009	0.002	—	—	—	2	0.015	0.003	—	—	—	—	—	—	22	0.033	0.002
4	5	0.013	0.001	3	0.021	0.001	2	0.023	0.001	4	0.015	0.002	2	0.015	0.001	24	0.025	0.004
5	3	0.018	0.002	5	0.020	0.001	2	0.016	0.001	2	0.021	0.001	2	0.015	0.000	9	0.038	0.003
6	7	0.025	0.001	6	0.034	0.002	2	0.038	0.002	2	0.017	0.000	3	0.023	0.001	—	—	—
7	6	0.028	0.002	8	0.041	0.001	4	0.030	0.005	2	0.017	0.000	3	0.027	0.000	—	—	—
8	2	0.030	0.000	5	0.035	0.004	3	0.039	0.004	4	0.021	0.001	2	0.024	0.001	24	0.034	0.003
9	4	0.032	0.001	3	0.031	0.002	2	0.030	0.003	2	0.033	0.001	4	0.031	0.001	8	0.047	0.001
10	6	0.032	0.002	3	0.042	0.001	3	0.038	0.002	2	0.028	0.000	3	0.030	0.002	—	—	—
11	3	0.038	0.003	3	0.039	0.005	5	0.049	0.002	4	0.028	0.000	2	0.032	0.001	—	—	—
12	4	0.039	0.001	3	0.045	0.002	2	0.043	0.004	—	—	—	—	—	—	27	0.058	0.004
13	5	0.050	0.003	6	0.059	0.002	3	0.052	0.002	2	0.041	0.000	3	0.039	0.001	16	0.052	0.002
14	2	0.061	0.001	5	0.066	0.003	2	0.065	0.002	3	0.044	0.001	4	0.046	0.005	—	—	—
15	6	0.064	0.002	5	0.071	0.003	4	0.063	0.003	2	0.047	0.000	4	0.048	0.002	45	0.076	0.005
16	5	0.069	0.003	6	0.076	0.003	2	0.069	0.002	3	0.059	0.000	3	0.059	0.000	5	0.087	0.002
17	3	0.077	0.002	2	0.084	0.001	2	0.074	0.002	4	0.061	0.002	4	0.055	0.000	7	0.079	0.003
18	5	0.081	0.002	3	0.092	0.002	2	0.080	0.001	4	0.069	0.005	4	0.063	0.002	6	0.074	0.005
19	4	0.101	0.002	3	0.103	0.000	2	0.098	0.001	4	0.060	0.001	4	0.073	0.004	14	0.095	0.002
20	4	0.117	0.003	3	0.136	0.004	3	0.131	0.003	4	0.070	0.004	5	0.081	0.006	12	0.096	0.004
21	7	0.179	0.004	4	0.198	0.004	2	0.186	0.014	7	0.132	0.004	7	0.150	0.006	3	0.136	0.004
22	4	0.259	0.004	3	0.267	0.002	2	0.261	0.001	6	0.194	0.013	5	0.222	0.016	13	0.175	0.013
23	2	0.016	0.001	3	0.022	0.002	—	—	—	2	0.010	0.000	2	0.015	0.000	13	0.018	0.002
24	4	0.114	0.004	—	—	—	—	—	—	—	—	—	—	—	—	7	0.121	0.004
25	Bureau of Standards	B. O. H. No. 15a;	S from 0.021 to 0.032	—	—	—	—	—	—	—	—	—	—	—	—	12	0.048	0.003
26	Bureau of Standards	B. O. H. No. 12b;	S from 0.018 to 0.025	—	—	—	—	—	—	—	—	—	—	—	—	14	0.026	0.002
27	Bureau of Standards	B. O. H. No. 13a;	S from 0.022 to 0.035	—	—	—	—	—	—	—	—	—	—	—	—	14	0.034	0.002
28	Bureau of Standards	B. O. H. No. 14a;	S from 0.031 to 0.041	—	—	—	—	—	—	—	—	—	—	—	—	14	0.039	0.003
29	Bureau of Standards	B. O. H. No. 16a;	S from 0.027 to 0.033	—	—	—	—	—	—	—	—	—	—	—	—	19	0.051	0.004

TABLE VIII.—DETAILED RESULTS OF ANALYSES.

Sample 1—Foundry Iron.

Nitric	Bamber's	Chloric	Dil. HCl	Conc. HCl
0.009	0.013	0.016	Direct	
0.008	0.017	0.012	0.009	Not run
0.006	0.017	Av. 0.014	0.009	
0.008	Av. 0.016	A. d. 0.002	Av. 0.009	
Av. 0.008	A. d. 0.002		A. d. 0.000	
A. d. 0.001			Annealed	
			0.009	
			0.008	
			0.009	
			Av. 0.009	
			A. d. 0.000	

Sample 2—Foundry Iron.

Nitric	Bamber's	Chloric	Dil. HCl	Conc. HCl
0.011	0.018	0.016	Direct	0.021
0.009	0.015	0.017	0.008	0.021
0.008	0.017	0.010	0.010	0.023
0.008	0.020	Av. 0.014	0.008	0.019
Av. 0.009	Av. 0.018	A. d. 0.003	0.007	0.018
A. d. 0.001	A. d. 0.002		Av. 0.008	0.021
			A. d. 0.001	0.023
Also				0.023
0.005			Annealed	0.023
0.004			0.010	Av. 0.021
0.007			0.009	A. d. 0.001
Av. 0.005			0.010	
A. d. 0.001			0.008	
			Av. 0.009	
Faster soln.			A. d. 0.001	
0.003				
0.002				
0.004				
Av. 0.003				
A. d. 0.001				
Quick soln.				
0.002				
0.002				
0.003				
Av. 0.002				
A. d. 0.000				

TABLE VIII.—DETAILED RESULTS OF ANALYSES.—(Continued)
Sample 3—"Vismara" from Inland Steel.

Nitric	Bamber's	Chloric	Dil. HCl	Conc. HCl		
0.007	Not run	0.012	Not run	0.034	0.031	
0.009		0.018		0.034	0.033	
0.012		Av. 0.015		0.033	0.030	
Av. 0.009		A. d. 0.003		0.033	0.037	
A. d. 0.002				0.035	0.033	
				0.034	0.035	
				0.034	0.029	
				0.034	0.029	
				0.034	0.031	
				0.033	0.029	
				0.032		
				0.033		
				Av. 0.033		
				A. d. 0.002		

Sample 4—Foundry Iron.

Nitric	Bamber's	Chloric	Dil. HCl	Conc. HCl		
0.015	0.021	0.023	Direct	0.024	0.028	0.020
0.013	0.022	0.022	0.013	0.026	0.026	0.019
0.013	0.021	Av. 0.023	0.016	0.024	0.028	0.031
0.013	Av. 0.021	A. d. 0.001	0.013	0.023	0.026	0.018
0.011	A. d. 0.001		0.018	0.021	0.022	0.019
Av. 0.013			Av. 0.015	0.024	0.031	0.032
A. d. 0.001			A. d. 0.002	0.023	0.032	0.020
					0.032	0.022
			Annealed			0.022
			0.014			
			0.015			
			Av. 0.015			
			A. d. 0.001			
				Total Av. 0.025		
				A. d. 0.004		

Sample 5—Mild Steel.

Nitric	Bamber's	Chloric	Dil. HCl	Conc. HCl		
			Direct	0.049		
0.017	0.021	0.015	0.021	0.034		
0.021	0.019	0.016	0.020	0.037		
0.017	0.019	Av. 0.016	Av. 0.021	0.037		
Av. 0.018	0.021	A. d. 0.001	A. d. 0.001	0.040		
A. d. 0.002	0.020		Annealed	0.036		
	Av. 0.020		0.015	0.038		
	A. d. 0.001		0.015	0.038		
			Av. 0.015	0.035		
			A. d. 0.000	Av. 0.038		
				A. d. 0.003		

TABLE VIII.—DETAILED RESULTS OF ANALYSES.—(*Continued*)*Sample 6*—Foundry Iron.

Nitric	Bamber's	Chloric	Dil. HCl	Conc. HCl
0.026	0.035	0.040	Direct	
0.025	0.030	0.036	0.017	Not run
0.026	0.035	Av. 0.038	0.017	
0.023	0.034	A. d. 0.002	Av. 0.017	
0.026	0.037		A. d. 0.000	
0.025	0.032			
0.024	Av. 0.034		Annealed	
Av. 0.025	A. d. 0.002		0.022	
A. d. 0.001			0.023	
			0.025	
			Av. 0.023	
			A. d. 0.001	

Sample 7—Foundry Iron.

Nitric	Bamber's	Chloric	Dil. HCl	Conc. HCl
0.023	0.043	0.023	Direct	
0.029	0.038	0.029	0.017	Not run
0.027	0.042	0.027	0.017	
0.031	0.041	0.040	Av. 0.017	
0.025	0.038	Av. 0.030	A. d. 0.000	
0.030	0.041	A. d. 0.005		
Av. 0.028	0.039		Annealed	
A. d. 0.002	0.042		0.027	
	Av. 0.041		0.027	
	A. d. 0.001		0.026	
			Av. 0.027	
			A. d. 0.000	

Sample 8—Iroquois Iron No. 3.

Nitric	Bamber's	Chloric	Dil. HCl	Corr. HCl		
0.030	0.041	0.034	Direct	0.039	0.038	0.034
0.030	0.038	0.043	0.023	0.029	0.032	0.035
Av. 0.030	0.028	0.041	0.022	0.038	0.035	0.036
A. d. 0.000	0.034	Av. 0.039	0.020	0.028	0.034	0.032
	0.032	A. d. 0.004	0.020	0.030	0.030	0.038
	Av. 0.035		Av. 0.021	0.036	0.035	0.039
	A. d. 0.004		A. d. 0.001	0.041	0.038	
			Annealed	0.023	0.036	
			0.023	0.034	0.031	
			0.024			
			Av. 0.024		Av. 0.034	
			A. d. 0.001		A. d. 0.003	

TABLE VIII.—DETAILED RESULTS OF ANALYSES.—(*Continued*)
Sample 9—Ship Plate.

Nitric	Bamber's	Chloric	Dil. HCl	Conc. HCl
0.032	0.032	0.033	Direct	0.044
0.031	0.028	0.027	0.033	0.047
0.032	0.034	Av. 0.030	0.032	0.046
0.034	Av. 0.031	A. d. 0.003	Av. 0.033	0.048
Av. 0.032	A. d. 0.002		A. d. 0.001	0.048
A. d. 0.001			Annealed	0.044
			0.032	0.048
			0.032	0.048
			0.030	Av. 0.047
			0.029	A. d. 0.001
			Av. 0.031	
			A. d. 0.001	

Sample 10—Am. Found. Assn. Stand. C, 2nd.

Nitric	Bamber's	Chloric	Dil. HCl	Conc. HCl
0.031	0.042	0.036	Direct	
0.036	0.041	0.039	0.028	Not run
0.030	0.041	0.040	0.028	
0.031	Av. 0.042	Av. 0.038	Av. 0.028	
0.030	A. d. 0.001	A. d. 0.002	A. d. 0.000	
0.028			Annealed	
Av. 0.032			0.029	
A. d. 0.002			0.029	
			0.033	
			Av. 0.030	
			A. d. 0.002	

Sample 11—Am. Found. Assn. Stand. D, 3rd.

Nitric	Bamber's	Chloric	Dil. HCl	Conc. HCl
0.042	0.031	0.042	Direct	
0.035	0.041	0.050	0.027	
0.036	0.045	0.050	0.028	Not run
Av. 0.038	Av. 0.039	0.051	0.028	
A. d. 0.003	A. d. 0.005	0.050	0.028	
		Av. 0.049	Av. 0.028	
		A. d. 0.002	A. d. 0.000	
			Annealed	
			0.031	
			0.033	
			Av. 0.032	
			A. d. 0.001	

TABLE VIII.—DETAILED RESULTS OF ANALYSES.—(Continued)

Sample 12—Bureau of Standards D, 6A and 6B; S ox. = 0.044 and 0.046.

Nitric	Bamber's	Chloric	Dil. HCl	Conc. HCl		
0.038	0.046	0.046		6b	6b	6a
0.040	0.042	0.039	Not run	0.062	0.058	0.062
0.037	0.046	Av. 0.043		0.057	0.062	0.055
0.039	Av. 0.045	A. d. 0.004		0.061	0.066	0.061
Av. 0.039	A. d. 0.002			0.062	0.047	0.056
A. d. 0.001				0.059	0.056	0.053
				0.048	0.045	0.060
				0.062	0.051	
				0.055	0.057	
				0.057	0.059	
				0.058	0.063	
					0.066	
					Av. 0.058	
					A. d. 0.004	

Sample 13—Am. Found. Assn. Stand. A, 2nd.

Nitric	Bamber's	Chloric	Dil. HCl	Conc. HCl	
0.052	0.057	0.052	Direct	0.051	0.049
0.051	0.056	0.049	0.041	0.048	0.053
0.045	0.058	0.054	0.041	0.051	0.051
0.053	0.059	Av. 0.052	Av. 0.041	0.055	0.049
0.047	0.062	A. d. 0.002	A. d. 0.000	0.050	0.050
Av. 0.050	0.063		Annealed	0.053	0.052
A. d. 0.003	Av. 0.059		0.038	0.052	0.052
	A. d. 0.002		0.039		0.057
			0.041		0.051
			Av. 0.039		
			A. d. 0.001		
				Av. 0.052	
				A. d. 0.002	

Sample 14—Foundry Iron.

Nitric	Bamber's	Chloric	Dil. HCl	Conc. HCl
0.060	0.069	0.063	Direct	
0.061	0.069	0.066	0.045	
Av. 0.061	0.068	Av. 0.065	0.044	Not run
A. d. 0.001	0.063	A. d. 0.002	0.043	
	0.063		Av. 0.044	
	Av. 0.060		A. d. 0.001	
	A. d. 0.003		Annealed	
			0.048	
			0.044	
			0.039	
			0.053	
			Av. 0.046	
			A. d. 0.005	

TABLE VIII.—DETAILED RESULTS OF ANALYSES.—(Continued)

Sample 15—Foundry Iron.

Nitric	Bamber's	Chloric	Dil. HCl	Conc. HCl		
0.063	0.068	0.059	Direct	0.069	0.089	0.069
0.060	0.075	0.064	0.047	0.069	0.071	0.068
0.063	0.073	0.061	0.047	0.074	0.076	0.074
0.062	0.067	0.068	Av. 0.047	0.076	0.087	0.083
0.067	0.071	Av. 0.063	A. d. 0.000	0.069	0.080	0.072
0.066	Av. 0.071	A. d. 0.003	Annealed	0.070	0.072	0.078
Av. 0.064	A. d. 0.003		0.050	0.081	0.080	
A. d. 0.002			0.050	0.071	0.077	
			0.048			
			0.045	0.067	0.074	0.062
			Av. 0.048	0.076	0.079	0.071
			A. d. 0.002	0.073	0.068	0.080
				0.071	0.075	0.080
				0.066	0.073	0.083
				0.076	0.067	0.084
						0.080
						0.079
						0.089
						0.087
						0.085
				Av. 0.076		
				A. d. 0.005		

Sample 16—Am. Found. Assn. Stand. B, 2nd.

Nitric	Bamber's	Chloric	Dil. HCl	Conc. HCl		
0.078	0.077	0.070	Direct	0.092		
0.065	0.069	0.067	0.059	0.087		
0.070	0.081	Av. 0.069	0.059	0.090		
0.067	0.080	A. d. 0.002	0.058	0.085		
0.070	0.075		Av. 0.059	0.088		
Av. 0.069	0.078		A. d. 0.000	Av. 0.087		
A. d. 0.003	Av. 0.076		Annealed	A. d. 0.002		
	A. d. 0.003		0.060			
			0.063			
			0.053			
			Av. 0.059			
			A. d. 0.004			

TABLE VIII.—DETAILED RESULTS OF ANALYSES.—(Continued)

Sample 17—Special Small Ingot.

Nitric	Bamber's	Chloric	Dil. HCl	Conc. HCl
0.075	0.084	0.076	Direct	0.072
0.076	0.083	0.072	0.061	0.084
0.079	Av. 0.084	Av. 0.074	0.061	0.084
Av. 0.077	A. d. 0.001	A. d. 0.002	0.064	0.080
A. d. 0.002			0.058	0.077
			Av. 0.061	0.080
			A. d. 0.002	0.076
			Annealed	Av. 0.079
			0.055	A. d. 0.003
			0.055	
			0.055	
			0.056	
			Av. 0.055	
			A. d. 0.000	

Sample 18—Special Small Ingot.

Nitric	Bamber's	Chloric	Dil. HCl	Conc. HCl
0.081	0.094	0.079	Direct	0.077
0.081	0.095	0.080	0.066	0.069
0.082	0.089	Av. 0.080	0.067	0.068
0.084	Av. 0.092	A. d. 0.001	0.080	0.085
0.078	A. d. 0.002		0.066	0.070
Av. 0.081			Av. 0.069	0.076
A. d. 0.002			A. d. 0.005	Av. 0.074
			Annealed	A. d. 0.005
			0.063	
			0.065	
			0.064	
			0.059	
			Av. 0.063	
			A. d. 0.002	

Sample 19—Special Small Ingot.

Nitric	Bamber's	Chloric	Dil. HCl	Conc. HCl
0.106	0.103	0.098	Direct	0.094 0.097
0.101	0.104	0.097	0.060	0.096 0.101
0.097	0.103	Av. 0.098	0.060	0.091 0.094
0.100	Av. 0.103	A. d. 0.001	0.058	0.095 0.093
Av. 0.101	A. d. 0.000		0.063	0.092 0.091
A. d. 0.002			Av. 0.060	
			A. d. 0.001	0.096
			Annealed	0.094
			0.075	0.094
			0.077	0.095
			0.072	
			0.066	Av. 0.95
			Av. 0.073	A. d. 0.002
			A. d. 0.004	

TABLE VIII.—DETAILED RESULTS OF ANALYSES.—(Continued)

Sample 20—Special Small Ingot.

Nitric	Bamber's	Chloric	Dil. HCl	Conc. HCl	
0.113	0.140	0.129	Direct		
0.116	0.138	0.128	0.074	0.092	0.092
0.121	0.131	0.136	0.066	0.085	0.090
0.119	Av. 0.136	Av. 0.131	0.074	0.096	0.090
Av. 0.117	A. d. 0.004	A. d. 0.003	0.065	0.096	0.093
A. d. 0.003			Av. 0.070	0.101	0.098
			A. d. 0.004	0.097	
			Annealed	0.111	
			0.088		
			0.086	Av. 0.096	
			0.086	A. d. 0.004	
			0.075		
			0.074		
			Av. 0.081		
			A. d. 0.006		

Sample 21—Special Small Ingot.

Nitric	Bamber's	Chloric	Dil. HCl	Conc. HCl	
0.176	0.179	0.199	Direct		
0.176	0.194	0.172	0.136	0.132	
0.182	0.195	Av. 0.186	0.131	0.134	
0.171	0.207	A. d. 0.014	0.127	0.141	
0.184	Av. 0.198		0.131	Av. 0.136	
0.182	A. d. 0.004		0.139	A. d. 0.004	
0.184			0.126		
Av. 0.179			0.132		
A. d. 0.004			Av. 0.132		
			A. d. 0.004		
			Annealed		
			0.158		
			0.141		
			0.155		
			0.156		
			0.152		
			0.137		
			0.151		
			Av. 0.150		
			A. d. 0.006		

TABLE VIII.—DETAILED RESULTS OF ANALYSES.—(*Continued*)*Sample 22*—Special Small Ingot.

Nitric	Bamber's	Chloric	Dil. HCl	Conc. HCl	
0.265	0.269	0.261	Direct	0.163	0.187
0.261	0.265	0.260	0.188	0.146	0.185
0.255	0.266	Av. 0.261	0.222	0.183	0.183
0.255	Av. 0.267	A. d. 0.001	0.190	0.169	0.186
Av. 0.259	A. d. 0.002		0.205	0.187	0.186
A. d. 0.004			0.188	0.186	
			0.172	0.142	
			Av. 0.194	0.177	
			A. d. 0.013	Av. 0.175	
			Annealed	A. d. 0.013	
			0.234		
			0.196		
			0.243		
			0.208		
			0.227		
			Av. 0.222		
			A. d. 0.016		

Sample 23—Foundry Iron.

Nitric	Bamber's	Chloric	Dil. HCl	Conc. HCl		
0.015	0.024		Direct			
0.016	0.020	Not run	0.010	0.018	0.014	0.019
Av. 0.016	0.023		0.010	0.016	0.018	0.020
A. d. 0.001	Av. 0.022		Av. 0.010	0.017	0.024	0.022
	A. d. 0.002		A. d. 0.000	0.014	0.020	
			Annealed	0.015		
			0.015	0.017		
			0.015	Av. 0.018		
			Av. 0.015	A. d. 0.002		
			A. d. 0.000			

Sample 24—High S Steel.

Nitric	Bamber's	Chloric	Dil. HCl	Conc. HCl	
0.120				0.125	
0.116	Not run	Not run	Not run	0.113	
0.109				0.116	
0.112				0.123	
Av. 0.114				0.119	
A. d. 0.004				0.123	
				0.124	
				Av. 0.121	
				A. d. 0.004	

TABLE VIII.—DETAILED RESULTS OF ANALYSES.—(*Continued*)*Sample 25*—Bureau of Standards B. O. H. No. 15a.

S from 0.021 to 0.032.

Nitric	Bamber's	Chloric	Dil. HCl	Conc. HCl	
				0.044	0.049
Not run	Not run	Not run	Not run	0.044	0.045
				0.042	0.048
				0.049	0.049
				0.053	0.047
				0.049	0.054
				Av. 0.048	
				A. d. 0.003	

Sample 26—Bureau of Standards B. O. H. No. 12b.

S from 0.018 to 0.025.

Nitric	Bamber's	Chloric	Dil. HCl	Conc. HCl	
				0.023	0.028
Not run	Not run	Not run	Not run	0.025	0.029
				0.026	0.027
				0.023	0.029
				0.024	0.028
				0.023	0.023
				0.023	0.025
				Av. 0.026	
				A. d. 0.002	

Sample 27—Bureau of Standards B. O. H. No. 13a.

S from 0.022 to 0.035.

Nitric	Bamber's	Chloric	Dil. HCl	Conc. HCl	
				0.034	0.034
Not run	Not run	Not run	Not run	0.033	0.036
				0.028	0.034
				0.035	0.033
				0.033	0.031
				0.035	0.039
				0.034	0.033
				Av. 0.034	
				A. d. 0.002	

Sample 28—Bureau of Standards B. O. H. No. 14a.

S from 0.031 to 0.041.

Nitric	Bamber's	Chloric	Dil. HCl	Conc. HCl	
				0.037	0.045
Not run	Not run	Not run	Not run	0.039	0.041
				0.036	0.044
				0.035	0.044
				0.036	0.038
				0.036	0.036
				0.037	0.039
				Av. 0.039	
				A. d. 0.003	

TABLE VIII.—DETAILED RESULTS OF ANALYSES.—(*Continued*)
Sample 29—Bureau of Standards B. O. H. No. 16a.

S from 0.027 to 0.033.						
Nitric	Bamber's	Chloric	Dil. HCl	Conc. HCl		
				0.045	0.049	0.054
				0.049	0.047	0.054
Not run	Not run	Not run	Not run	0.051	0.054	0.056
					0.044	0.052
					0.044	0.057
					0.049	0.057
						0.055
						0.055
						0.052
						0.049
				Av. 0.051		
				A. d. 0.004		

THE PRECISION OF RESULTS.

Chemical determinations vary greatly as to the precision which can be attained and the sulfur determination is one of those which combined circumstances have placed amongst the least precise.

The relative difficulty of making sulfur determinations may be illustrated by comparing student results on silicon and sulfur. A foundry iron containing 3.56 per cent. silicon and 0.021 per cent. sulfur was analyzed by eight students with the following figures:

Student	Silicon	Sulfur
A	3.66 and 3.59	0.015 and 0.017
B	3.54 and 3.45	0.008 and 0.010
C	3.53 and 3.49	0.055 and 0.053
D	3.56 and 3.53	0.033 and 0.033
E	3.66 and 3.67	0.010 and 0.010
F	3.33 and 3.45	0.028 and 0.035
G	3.50 and 3.50	0.027 and 0.028
H	3.43 and 3.46	0.040 and 0.040

Evidently students can easily attain a precision of one part in thirty in determining silicon but they may be a hundred per cent. either too high or too low in their sulfur results.

The regrettable uncertainty in the sulfur analysis is prominent in the professional field and every now and then presents some striking discrepancy. One is reminded of the sample which Cly-

mer sent about in 1892 whose sulfur was reported all the way from 0.005 to 0.024 per cent.; of the several announcements about the year 1903 that samples lost sulfur on standing, and of current statements on some Bureau of Standards samples, "The values reported for sulphur by evolution were too discordant to be of value."

The actual precision to be expected in the best professional work with a highly detailed procedure and using average figures appears to be of the order of from one part in five to one part in forty; illustrations are available in the certificates of analyses which accompany the Bureau of Standards samples.

TABLE IX.—AVERAGE RESULTS ON STANDARD SAMPLES.

Analyst	Standard iron B 2nd (No. 16 in text)	Standard iron C 2nd (No. 10 in text)	Standard iron D 3rd (No. 11 in text)
A	0.070	0.036	0.032
B	0.073	0.035	0.035
C	0.069	0.032	0.038
D	0.072	0.033	0.031
E	0.068	0.032	0.038

Analyst	Standard iron 6a and 6b (No. 12 in text)	Standard steel 20a	Standard steel 21a
1	0.048	0.026	0.036
2	0.050	0.029	0.033
3	0.046	0.026	0.033
4	0.044	0.021	0.032
5	0.048	0.029	0.041
6	0.042	0.026	0.031
7	0.044	0.028	0.035
8	0.046	0.032	0.036
9	0.048	0.029	0.036
10	0.047	—	—

As these are the average results as obtained by prominent analysts for the Bureau, the figures probably agree much better than might be expected of the average analyst on ordinary work; if the true amount is assumed as the mean of the individual averages the percentage deviations are of course much less than should the correct amount be at one of the extremes.

The necessary fundamental conditions which shall assure uniformity and precision by different operators may be stated briefly:

1. Samples must be from a lot whose sulfur is uniformly distributed in the solid metal; divisions of the lot must be made accurately. (A riffle cutter and several hundred cuts into two halves is quickest and best.)

2. The analytical method must not lose sulfur either in any way, such as with escaping gases or insoluble in a residue.

3. The analytical method must not be susceptible of gaining sulfur, as by excessive number or amount of reagents, by numerous transfers or tedious evaporations, ignitions and filtrations.

4. The final measurement should be inherently much more precise than the determination and independent of comparisons or reference to a standard sample; a weighing of a comparatively pure barium sulfate or an iodine titration standardized to pure sodium oxalate are both satisfactory.

The notes already written on the different methods embody the principles and justify the author's conclusion that the evolution method should be adopted as a standard method. The solvent should be concentrated hydrochloric acid, the apparatus should internally condense as much acid as possible and should be entirely of glass. Any method involving solution in nitric acid will always be subject to loss of sulfur in the fumes; any method requiring precipitation in a large receptacle, or the filtration of a bulky precipitate or the elapse of a considerable interval of time will be subject to vitiating influences.

The evolution method offers the best conformity with the fundamental requirements. The reagents and chemicals used in the evolution method can all be tested in stock solutions in large bulks and preserved indefinitely. The sample is practically perfectly separated from the operator, the dust and fume of the laboratory and from accidents during the liberation and measurement of the sulfur. The single transfer is from a closed flask to a beaker and the entire elapsed time need not exceed 20 minutes from weighing sample to reporting result.

The evolution method breaks down with very high sulfur material; doubtless this can be overcome. High sulfur stock will also probably separate elemental sulfur upon treatment with nitric acid and so require special attention by an oxidation method.

The figures recorded in Table VII and Table VIII indicate that samples running very low in sulfur by oxidation methods give much higher results by the proposed evolution method. The amount of cadmium sulfid precipitated in the beaker supplies a visual method of estimating the sulfur content of the material, especially with small percentages of sulfur. There is hardly a possibility but that samples 2, 3, 4 and 5 contained more than 0.020 per cent. sulfur yet each gave less than 0.020 per cent. by the most careful nitric acid oxidation method. As blanks were run before, during and after the samples with every condition constant except the presence of the sample in the flask and as the proper amount of cadmium sulfid precipitated in the beaker there is every reason to consider the sulfur as having come from the sample.

Constant Errors.

The small amount of sulfur to be accounted for in determining that element in iron and steel allows influences of commonly inconsequential importance to effect the results enormously. Good instances of factors leading to constant errors are:

1. Volatilization losses when dissolving in nitric acid.
2. Dust increasing the sulfur when using Bamber's method.
3. Cumulative effect of sulfur in reagents.
4. Standard samples not comparative with unknown samples.
5. Incomplete blanks with the evolution method.
6. Precipitation of sulfur in large volume of dilute acid.
7. Applying an imaginary "constant" correction to all results.
8. Incomplete generation of H_2S by using diluted acid.

The literature on sulfur determination is hardly more than one continued discussion on "constant errors." Every attempt to apply any sort of general correction has been an abject failure. Plainly there is the greatest urgency for standardization of conditions before an analysis can be rationally started; the all-glass condensing evolution flask has been the greatest step toward

standardizing conditions and has evidently been widely adopted in European countries with the greatest satisfaction. No other suggested method has even approached the improved evolution method in the minimum of conditions to arbitrarily regulate, in seclusion of the analysis from external circumstances and in high and unimpeachable results.

Chance Errors.

The sulfur determination in all forms but the evolution process is highly susceptible of chance errors and accidents. The solution of the sample in concentrated nitric acid does not commonly take place smoothly and quietly without extreme skill in warming and chilling. Some samples dissolve with great violence, others act alternately passive and explosively. Samples are frequently lost by boiling over or too rapid solution; the best work demands that any unruly lot be discarded promptly and others started.

The effect of segregation in the sample is similar to a chance error and indistinguishable from an error happening during the analysis. But original segregation is no analytical error and is often fully as important a fact to be made aware of as the average per cent. of sulfur; on this account the author has suggested that the results of apparently perfect yet discordant analyses should be reported to indicate the extreme ranges of sulfur content found.

Chance errors are unavoidable by any method; work of precision therefore requires as many determinations as convenient to establish a probable sulfur content. Work to establish the value of a standard material or for comparison of methods or in important cases should have many individual lots run. The present study is lamentably lacking in simply the number of determinations made on the samples investigated; yet the making of a thousand determinations, many of them by the chloric acid method and Bamber's method, is an undertaking of several months duration.

Distribution of Results.

The numerical average of a series of determinations is a figure quickly and simply obtained; that this average may indicate even

a probable result depends entirely on the distribution of the several measurements.

To most effectively illustrate the significance of the distribution of results the figures obtained on samples 4, 8, 13, 15 and 19 have been plotted in Table X. These samples were chosen because more results were obtained on them than the others.

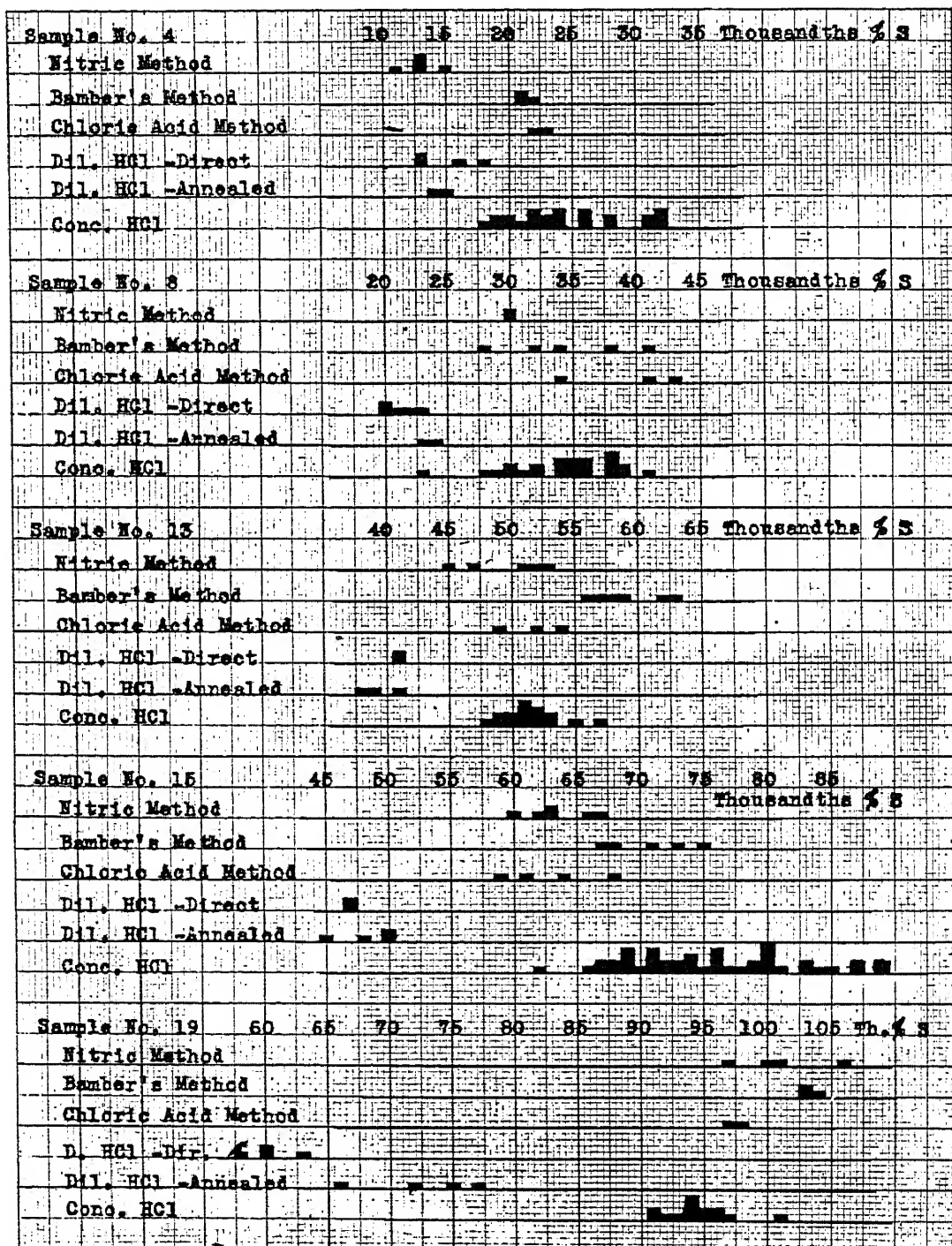
In only three instances of the thirty indicated are there enough results or are they suitably arranged to indicate the probable result with a precision of 0.001 per cent. A determination is represented by a block in black two spaces wide and one space high. In the nitric acid method for sample 4 the blocks concisely indicate a maximum at 0.013 per cent.; sample 13 by the concentrated acid evolution method there is again a well established maximum indicated at 0.051 per cent.; again, in sample 19 by the dilute evolution method, direct, a maximum or probable result of 0.060 per cent. is indicated.

Most of the recorded plots indicate merely a range in results and whether the maximum is to come at one or another thousandth per cent. is a matter which can be determined only by getting more results. The best example of the indcision is in sample 15 where 45 results were gotten by the concentrated acid, evolution method. However simply the average may figure to 0.076 per cent. and the probable error placed at 0.004 per cent., by the theory of least squares, the inspection of the plot shows that no satisfactory precision has been gained by the 45 analyses. It looks as if three or four hundred analyses would have to be made to establish the probable result within 0.001 per cent.

A complete and convincing comparison of methods or precise result on any given sample should have the results accumulated until the most probable result is demonstrated by a clean-cut and conspicuous maximum. As long as too much uncertainty attaches to a final figure there should be no hesitation about doing more analyses; the evolution method affords an especially rapid and cheap and standardized process. It is suggested that in the reports on standard samples the actual results as obtained by the respective analysts should be plotted as in Table X. A frank disclosure

of the status of the determination can only improve the methods, raise the standard of analytical work and react favorably on the entire metallurgical industry which uses the analysis.

TABLE X.—DISTRIBUTION OF RESULTS.



BIBLIOGRAPHY.

- 1797—VAUQUELIN, C. *J. des Mines*, Vol. 5, p. 3-32. "Analyse de quatre échantillons d'aciers, avec des Réflexions sur les moyens nouveaux employés pour cette analyse."

Analyses of four steels:

	I.	II.	III.	IV.
Carbone	0.00789	0.00683	0.00789	0.00631
Silice	0.00315	0.00273	0.00315	0.00252
Phosphore	0.00345	0.00827	0.00791	0.01520
Fer	0.98551	0.98217	0.98105	0.97597
	<u>1.00000</u>	<u>1.00000</u>	<u>1.00000</u>	<u>1.00000</u>

He says Bergmann (1735-1784) is credited with having first devised methods to analyze iron and steel, that they have been little changed since Bergmann proposed them, and that they are inexact. Vauquelin presents the analyses after much difficulty and many troubles. A little later (1806) when analyzing irons Vauquelin finds C, P, Mn, Cr, and Al in the materials and remarks about the smell during solution, saying that it cannot be wholly due to the P, but he does not mention S or H₂S.

- 1803—VAUQUELIN, C. *J. des Mines*, Vol. 13, p. 308. Analyzing meteorites Vauquelin finds them composed of silica, iron oxid, magnesia, nickel and sulfur. The sulfur separates as a globule with HNO₃ or as H₂S with HCl; Vauquelin considers the sulfur combined with the iron and nickel but makes no quantitative determination.

- 1805—ROZIERES, M. *J. des Mines*, Vol. 17, p. 35. "Sur l'emploi de la houille brute dans les diverses opérations de la fabrication du fer." On page 46 Rozieres remarks that when steel is heated with crude oil flame the sulfur from the oil enters the metal and makes it red short.

- 1806—BLACK, JOSEPH. "*Elements of Chemistry*," Phil., 1806; Vol. III, p. 204. "Professor Bergmann made a great num-

ber of experiments to learn the causes of these different qualities [cold- and red-shortness] of iron; and thought he had discovered the cause of the cold-shortness, ascribing it to the presence of a metal which he called *siderum*; but this has been found to be a mistake. Mayer showed that it is a phosphat of iron. Mr. Cort's process removes or prevents this bad quality." No mention of sulfur to be found.

1807—GUENYVEAU, M. *J. des Mines*, Vol. 22, p. 439. "Analyse de quelques Minerais de fer et Produits de fourneau du Creusot."

The following analyses given without methods:

	Gray pig	Another (better)
Si	3.5	0.54
Al	0.8	Tr
Ca	0.5	—
S	0.3	No
P	0.75	0.27
C	2.10	2.40
Mn	Tr	—
Cr	No	Un peu
Fe, metallic	93.15	96.79
	<hr/> 100.00	<hr/> 100.00

1808—BERTHIER, M. *J. des Mines*, Vol. 23, p. 177. "Analyses de quelques produits de forges et de hauts fourneaux." Also in Karsten's "*Archiv für Bergbau und Hüttenwesen*," Vol. 7, p. 333 (1823).

	Pig St. Helena	Pig Alleward	Pig Hartzerrennen
Slag	1.7	2.2	0.0
Sulfur	0.0	Tr	0.0
Carbon	1.0	3.0	0.5
Manganese	1.5	1.8	0.4
Copper	0.1	0.2	0.3

Methods of analyses not stated; says they have already been published.

- 1840—BERZELIUS, J. *Central Blatt*, Vol. 11, p. 746. "Methode Eisen und Stahl zu analysieren, von Berzelius." *Berz. Jahresbericht*, Vol. 19, pp. 281-288.

Evolution method using HCl; H_2S is absorbed in $AgNO_3$; S weighed as $BaSO_4$. Dissolves samples in $CuCl_2$ soln. for C detn.

- 1842—BROMEIS, C. *Ann. de Chem. und Pharm.*, Vol. 43, p. 241. "Ueber den Kohlenstoffgehalt des Eisens und seine Bestimmung." Also in *Central Blatt*, Vol. 13, p. 917 (1842), and *Chemical Gazette*, Vol. 1, p. 180 (1842).

Dissolves the iron in dilute H_2SO_4 , absorbs H_2S in ammoniacal $AgNO_3$ soln. Statement is merely note at end of article on carbon determination.

- 1847—PRECHTL, JOH. JOS. "Technologische Encyklopädie oder alphabetisches Handbuch." Stuttgart, 1847. Vol. 15, pp. 306 to 576 gives a most thorough discussion of steel with hardly a mention of sulfur. The following analyses of materials are given:

	Iron	Carbon	Manga- nese	Silicon	Nitrogen	Copper	Tin	Phos.
	97.114	2.171	0.005	0.182	0.532	—	—	—
	95.135	3.182	0.221	0.533	0.927	—	—	—
	94.057	4.258	0.850	0.084	0.749	—	—	—
	94.576	3.721	0.9975	0.1201	0.5842	—	—	—
Spiegeleisen	88.961	5.440	4.003	0.171	1.200	0.166	0.116	—
							Arsenic	
South Wales iron	98.904	0.411	0.043	0.084	—	0.000	0.000	0.401
Dannemora iron	98.775	0.843	0.054	0.118	—	0.068	0.017	0.000
Cement steel bar	98.018	1.713	0.023	0.122	—	0.067	0.008	—
Forged steel	98.325	1.431	0.020	0.120	—	0.066	0.007	—
Poured steel	97.943	1.724	0.020	0.215	—	0.065	0.007	—

- 1849—WRIGHTSON, F. C. *Chemical Gazette*, Vol. 7, pp. 478-484. "On the Analyses of some Specimens of Hot and Cold Blast Iron." Also in *J. Chem. Soc.*, London, Vol. 1, p. 331.

For sulfur determination he treats 20 to 30 grams of sample with fuming HNO_3 ; separates SiO_2 by evaporating,

heating, and taking up with HCl. BaCl_2 soln. is added to the HCl soln. and after standing 24 hours the BaSO_4 is filtered off, ignited and weighed.

These are the first sulfur analyses published which appear at all reliable.

	Grade	Iron	Carbon	Manga- nese	Silica	Nitrogen	Sulfur	Phos.	Total
Cold Blast	2	92.98	2.31	0.49	3.51	—	0.99	0.47	100.75
	4	90.61	2.19	0.91	3.45	—	0.30	0.41	97.87
	6	93.53	2.04	0.95	1.79	0.25	0.39	0.31	99.26
	8	95.67	1.79	0.35	1.37	—	0.36	0.20	99.74
Warm Blast	2	92.45	1.96	0.54	3.09	—	0.57	0.40	99.01
	4	91.82	2.76	0.91	2.89	—	0.26	lost	98.64
	6	94.20	2.11	0.50	1.33	—	0.20	0.54	98.88
	8	95.08	2.28	0.79	1.57	—	0.45	0.38	100.55
Hot Blast	2	90.76	2.87	0.79	5.14	tr	1.07	0.51	101.14
	4	91.30	2.09	0.69	5.06	—	0.28	0.55	99.97
	6	94.31	1.82	0.79	1.57	—	0.20	0.50	99.19
	8	95.64	1.59	0.39	1.34	0.10	0.33	0.71	100.10

1852—JANOYER, M. *Annalen des Mines*, Feb., 1852. Copied in *Chemical Gazette*, Vol. 10, pp. 227-235. "On the Influence of Sulphur upon the nature of Cast Irons."

He determines sulfur by dissolving in aq. reg., prec. with BaCl_2 and weighing BaSO_4 .

1853—MORFIT, CAMPBELL, and BOOTH, JAMES C. *Chemical Gazette*, Vol. 11, pp. 368-378, 388-398, 411-413. "On the Analysis of Cast Iron." Pages 411-413 are on the determination of sulfur, arsenic and antimony.

They dissolve 5 grs. of clippings in 1 oz. of pure nitric acid with boiling; 13 to 15 grs. of KClO_3 are added and soln. evap. to dryness. Residue is taken up in HCl, diluted, and filtered. BaCl_2 soln. is added, stirred and left from several days to 1 week, after which the ppt. is filtered off, washed, ignited, and weighed.

They say aqua regia is not as good a solvent because sulfur compounds may be volatilized.

1856—GURLT, A. *Polytechn. Centrallbl.*, 1856, pp. 366-379. Copied in *Chemical Gazette*, Vol. 14, pp. 230-236 and 254-260. "On the Compounds of Carbon and Iron, and their Influence on the Production of Pig Iron." On p. 260 writes of sulfur determination.

Don't precipitate sulfur from nitrate soln. with Ba salt for $\text{Ba}(\text{NO}_3)_2$ comes down, too. Better to dissolve 1 gram of sample in dil. H_2SO_4 leading H_2S into dil. soln. of lead acetate, filter, wash, oxidize with HNO_3 to PbSO_4 which is weighed.

Analyses by Karsten, Berthier, Bodemann, Bromeis, Wrightson and Miller are given. The structure of iron is worked out from analyses.

COMPOSITION OF 5 SCOTCH IRONS.

	1	2	3	4	5
Carbon	1.347	1.021	1.793	1.925	2.451
Graphite	3.156	2.641	1.110	1.051	0.877
Silicon	2.721	3.061	2.165	1.895	1.124
Sulfur	1.267	1.139	1.480	1.614	2.516
Phosphorus	0.842	0.928	1.171	1.811	0.913
Iron	88.983	90.236	89.314	91.368	89.863
Manganese	2.401	0.834	1.596	0.571	2.715
Total	100.717	99.860	98.629	100.235	100.459

1856—NICHOLSON, E. CHAMBERS, and PRICE, D. S. *Phil. Mag.*, 4th Series, Vol. 11, pp. 169-172. "Remarks on the Estimation of Sulphur in Iron, and on the Solubility of Sulphate of Baryta in Nitric Acid."

Also in: *Central Blatt*, (1856), 426, and
Jahresbericht, (1856), 9, 729.

Criticism and experiments with HNO_3 oxidation method. They find H_2SO_4 in the nitric acid and that BaSO_4 is slightly soluble in dil. HCl . They find that HNO_3 or aq. reg. methods give *high* results. For correct results they use evolution method, weighing S as PbS . By fusion of residues find only trace of sulfur.

1857—NOAD, HENRY M. *J. Chem. Soc.*, Vol. 9, p. 15. "Note on the Solubility of Sulphate of Baryta in Hydrochloric Acid."

	H ₂ O grains	HCl(1.153) grains	K ₂ SO ₄	Ba(NO ₃) ₂	BaSO ₄
1	1,000	0	5 grains	10 grains	6.74 grains
2	900	100	5 "	10 "	6.70 "
3	800	200	5 "	10 "	6.71 "
4	700	300	5 "	10 "	6.72 "
5	600	400	5 "	10 "	6.69 "
6	500	500	5 "	10 "	6.71 "
7	400	600	5 "	10 "	6.78 "
8	300	700	5 "	10 "	6.77 "
9	200	800	5 "	10 "	6.76 "
10	100	900	5 "	10 "	6.78 "
11	0	1,000	5 "	10 "	6.78 "
12		500	5 "	10 "	6.78 "

He finds BaSO₄ somewhat soluble in a large bulk of HCl but not soluble enough to affect results when using dil. HCl. He finds Ba(NO₃)₂ carried down mechanically. Advises about looking for H₂SO₄ in HNO₃.

For S in crude irons uses evolution method dissolving with dil. HCl. The H₂S is caught in HCl soln. of As₂O₃ and weighed as AsS₃. P does not interfere. Lead nitrate or acetate soln. may also be used.

1860—EGGERTZ, V. *Jern-Kontorets Annaler*, Vol. 15, pp. 11-19. "Om bestämmandet af Svafvelhalten hos jern och jern-maler."

Also in: *Dingl. Polyt. J.*, Vol. 164, p. 186 (1862).

Jahresbricht, Vol. 15, p. 572.

Berg. u. Hütt. Zeit., Vol. 21, p. 88 (1862).

5 grams of sample sieved through 0.6 mm. holes is added to 10 grs. of KClO₃ in 200 cc. H₂O in 500 cc. flask. When boiling add 60 cc. HCl, 1.12. S may swim on surface. Filtered liquid in 50 cc. vol. has 2 cc. sat. BaCl₂ soln. added. Add NH₃ to cooled soln., stand 24 hrs., decant, filter, wash, dry, ignite, weigh. If ppt. is red treat with HCl and repeat.

He also uses evolution method, colorimetric on silver foil.

1862—ABEL, F. A. *Chemical News*, Vol. 6, p. 124. "On the Chemical Examination of Iron Samples, and of the Materials Employed in their Manufacture."

"Sulphur.—100 grains of the iron borings were slowly dissolved in concentrated hydrochloric acid, the evolved gas being passed through a solution of acetate of lead, slightly acidified with acetic acid, the sulphuretted hydrogen, disengaged together with the hydrogen, precipitated the sulphide of lead, which was collected on a filter, washed, burnt, and subsequently (in the customary manner) converted into sulphate of lead, from the weight of which the percentage of sulphur was calculated."

1862—NICKLÈS, J. *J. de Pharm. et de Chim.*, Vol. 42, p. 273. "De l'analyse de la fonte et de l'acier. Recherche du soufre et du phosphore dans ces métaux."

Also in: *Chemical News*, Vol. 7, pp. 87-88 (1863).

Central Blatt, (1863), p. 287.

Compt. Rend., Vol. 55, p. 503.

Jahresbericht, (1862), p. 604.

Zts. für anal. Chem., Vol. 2, p. 438.

Repert. chim. appl., (1862), p. 872.

The iron sample is dissolved and the sulfur oxidized by bromine solution; after filtering off graphite and precipitating with BaCl_2 soln. the BaSO_4 is obtained and weighed.

He reduces the iron to a fine powder by filing or a steel mortar, a difficult operation and apt to make the sample too small.

He also finds that bromine in pure water has energetic attack on pieces of metal weighing several grams, thus a piece of cast iron weighing 15 grams was dissolved in 40 mins.

1863—LIPPERT, G. *Zts. f. anal. Chem.*, Vol. 2, p. 39. "Beiträge zur Analyse des Roheisens."

Also in: *Central Blatt*, (1863), p. 1064.

Jahresbericht, Vol. 16, p. 690.

Working under Fresenius he prefers evol. method on 10 grs. of sample, the H_2S is caught in a lead soln., oxidized by KNO_3 with a fusion, the H_2SO_4 is extracted and weighed as BaSO_4 . The aq. reg. method is not recommended; evaporations are tedious, BaSO_4 is sol. in excess of acids, BaSO_4 not sol. in neutral FeCl_3 , but basic sulfates separate.

Analyses of spiegeleisen :

Fe	82.860	As	0.007
Mn	10.707	Sb	0.004
Ni	0.016	P	0.059
Co	Tr	S	0.014
Cu	0.066	Si	0.997
Al	0.077	C	4.323
Ti	0.006	O_2 (SiO_2)	0.475
Mg	0.045	O_2 (Al_2O_3 , FeO , CaO, MnO, MgO, Na, K, Li)	0.190
Ca	0.091		
K	0.063		
Na	Tr		
Li	Tr		

Total = 100.014

1867—FORBES, D. *Chemical News*, Vol. 16, p. 105. "Analysis of Blister Steel." Also in *Central Blatt*, (1869), p. 36.

"Determination of the Sulphur.—107.58 grains were placed in a flask provided with a safety-funnel, and digested (for twenty-four hours) in the cold with strong hydrochloric acid; the gas evolved was passed through a solution of pure chloride of zinc supersaturated with ammonia; the iron being all dissolved, the zinc solution was boiled with nitric acid in some excess, nearly neutralized by ammonia to prevent any solvent action from excess of acid, and precipitated by a solution of pure chloride of barium, 0.04 grain of sulphate of barytes were obtained, equivalent to 0.005 per cent. of sulphur in the steel."

ANALYSIS

Carbon, combined	0.627
Carbon, graphitic	0.102
Silicon	0.030
Phosphorus	0.000
Sulphur	0.005
Manganese	0.120
Iron, by difference	99.116

1867—TOSH, E. G. *Chemical News*, Vol. 16, p. 168. "On the Analysis of Cast Iron."

3 grams of sample dissolved in HNO_3 with little HCl , evap. to dryness; take up with HCl , dilute, filter, add BaCl_2 soln. and let stand 24 hours (remove Fe from ppt. with dil. HCl) before filtering, washing, igniting and weighing BaSO_4 .

1867—EGGERTZ, M. W. *Moniteur Scientifique*, Series 2, Vol. 4, pp. 1080-1081. "Memoire sur le dosage du soufre dans le fer et ses mineraux."

Also in: *Chemical News*, Vol. 17, p. 207 (1868), and

Chemical News, Vol. 18, pp. 15-17.

Bull. Soc. Chim., Vol. 9, p. 370.

Gives oxidation method as under previous reference of 1860.

For colorimetric detn. prepares 0.1 gr. of fine sample by pulverizing and sieving through 0.6 mm. holes and placing in jar 15 cm. by 5 cm. with 1 gr. H_2O and 0.5 gr. conc. H_2SO_4 (better, 1.5 grs. H_2SO_4 , 1.25 sp. gr.); a silver plate (25 per cent. Cu) is suspended inside on a wire for 15 minutes after which it is removed and the color compared with standards. Many precautions are mentioned.

E. observes that sulfur is not evenly distributed throughout a piece of iron, varying considerably in different places.

E. says: "Many circumstances appear to show that the quantity of sulfur in iron diminishes with time, at least on the surface, and under favorable circumstances."

1868—GINTL, M. W. *J. Prak. Chem.*, Vol. 105, pp. 114-117, and *Ztschr. anal. Chem.*, Vol. 7, p. 427. "Ueber die Bestimmung des Schwefelgehaltes in Roheisen."

Also in: *Bull. Soc. Chim.*, Vol. 11, p. 239 (1869).

Central Blatt, (1869), p. 25.

Wien. Sitzungsber., (1869), p. 58.

Polyt. Jour., Vol. 190, p. 113.

Jahresbericht, (1868), p. 851.

As S is left in the residues by oxidation and evolution methods G. finely pulverizes the sample and then treats 8 to 10 hours with 20 parts of conc. FeCl_3 soln. which dissolves the Fe and leaves a residue to fuse with a mixture of 3 parts KNO_3 and 1 part KOH . From the fusion the SO_4 is pptd. as BaSO_4 .

	By Lippert's method	Gintl's method
A	0.197% S	0.201% S
	0.178	0.189
	Av. = 187%	Av. = 195%
B	0.342% S	0.360% S

1870—HAMILTON, H. B. *Chemical News*, Vol. 21, p. 147. "Determination of Sulphur in Irons."

Also in: *Zeit. anal. Chem.*, Vol. 9, p. 508.

Bull. Soc. Chim., Vol. 14, p. 214.

Jahresbericht, (1870), p. 945.

A modification of the method given in Fresenius' "Quantitative Analysis;" uses evolution method with somewhat dil. HCl collecting H_2S in KOH , oxidizing with Cl and weighing as BaSO_4 . H. treats the residue with aq. reg. and obtains further BaSO_4 to add to main ppt.

For puddle bars uses 10 grams of sample.

	1st. analysis	2nd analysis	Diff.
Sample No. 1.....	0.038	0.026	0.012
Sample No. 2.....	0.088	0.073	0.015
Sample No. 3.....	0.045	0.033	0.012

1870—RICHTERS, E. *Ding. Polyt. J.*, Vol. 197, pp. 168-171. "Zur Bestimmung des Schwefels, Phosphors und Siliciums in Roheisen."

Also in: *Chemical News*, Vol. 22, p. 144 (1870).

Central Blatt, (1871), p. 154.

Ztschr. anal. Chem., Vol. 10, p. 370.

Jahresbericht, (1870), p. 943.

Reviews methods and combinations; thinks Gintl's method best as P can be det'd in residue.

	Gintl's method	Lippert's method	Residue	Total
Sample 1	0.0604% S	0.0333% S	0.0230% S	0.0562% S
2	0.0604	0.0300	not det'd	
3	0.0133	Tr	0.0090	—
4	0.0302	0.0150	0.0140	0.0290

1870—KONINCK, L. L., and KONINCK, L. L., and DIETZ, E. *Revue Univ. des Mines*, Vol. 28, p. 402, and Vol. 28, p. 406. "Dosage du soufre dans la fonte: Procédés nouveaux par L. de Koninck.

Also in: *Chemical News*, Vol. 23, p. 204.

Ztschr. anal. Chem., Vol. 31, p. 705.

Reviews old methods and then proposes two new ones.

1. Evolution method has H_2S absorbed in AgNO_3 , the Ag_2S is oxidized with Br , the AgBr is removed and the SO_4 pptd. with BaCl_2 .

2. Evolution method has H_2S absorbed in neutral cadmium solution and the acid liberated is titrated with KOH .

1871—MEINEKE, K. *Ztschr. anal. Chem.*, Vol. 10, pp. 280-284. "Bestimmung des Phosphor- und Schwefel-Gehaltes in Eisen."

Also in: *Jahresbericht*, (1871), p. 881.

J. Chem. Soc., Lond., Vol. 25, p. 89 (1872).

Dissolves sample in acid CuCl_2 and NaCl solution; 5 grs. dissolves in 1.5 hours, much quicker than Gintl's FeCl_3 . Filters off residue, oxidizes with HNO_3 and KClO_3 , evaporates, takes up in water and ppts. BaSO_4 which is weighed.

Equations: $\text{FeS} + \text{CuCl}_2 = \text{FeCl}_2 + \text{CuS}$.

$\text{CuS} + \text{CuCl}_2 = \text{Cu}_2\text{Cl}_2 + \text{S}$

	Evolution method	New method
Iron	0.118	0.118
Steel	0.055	0.064
Steel	0.052	0.060
Steel	0.053	0.060
Steel	0.087	0.090

1871—ELLIOTT, ARTHUR H. *Chemical News*, Vol. 23, p. 61 and 143. "On the Determination of Sulphur in Cast Iron."

Also in: *J. Chem. Soc. Lond.*, (1871), I, p. 159.

Central Blatt, (1871), p. 2 and p. 343.

Poly. Jour., Vol. 199, p. 390.

Ztschr. anal. Chem., Vol. 11, p. 105 (1872).

H₂S evolved by dil. HCl is absorbed in NaOH and on acidification is titrated with standard iodine soln. The second communication says the HCl solution contains no SO₄ and that mere traces of S remain in the insoluble residue. Uses flask with funnel and test tube; rubber connections.

Results on 2 samples:

A	B
0.136	0.077
0.120	0.072
0.136	0.080
0.119	0.076
0.130	0.085
	0.083
	0.081

1872—PETERS, S. *Chemical News*, Vol. 25, p. 11. "Sulphur Estimation in Cast Iron by Mr. A. H. Elliott's Method."

Finds sulfur left in residue by Elliott's method when residue is fused and BaCl₂ added to solution. Doubts value of method with irons and steels high in carbon.

1872—ELLIOTT, A. H. *Chemical News*, Vol. 25, p. 35. "A. H. Elliott's Method for Sulphur in Cast Iron."

Replying to S. Peters says he compared evolution method with Wöhler's chlorine method and the CuCl₂ method and finds evolution easiest and giving most concordant results. It is true his samples did not contain much combined carbon; residual sulfur will be found inappreciable.

1872—MORRELL, T. T. *American Chemist*, Vol. 3, p. 180. "Estimation of Sulphur in Iron and Steel."

Also in: *Chemical News*, Vol. 28, p. 229 (1873).

J. Chem. Soc. Lond., Vol. 27, p. 187 (1874).

Central Blatt, (1873), p. 282.

Jahresbericht, (1872), p. 822.

Dissolves sample in HCl, H_2S is absorbed in ammonia. Cd soln., the ppt. is dried and weighed. PH_3 without influence. A bessemer steel of 0.13 per cent. S gave these results:

0.124% S

0.125

0.137

0.125

0.124

1873—PIESSE, CHARLES H. *Chemical News*, Vol. 28, p. 248.

"On the Estimation of Sulphur in Pig Irons, etc."

Also in: *Bull. Soc. Chim.*, Vol. 21, p. 68 (1874).

J. Chem. Soc. Lond., Vol. 27, p. 391 (1874).

To 3.5 to 4 grs. sample in 300 cc. beaker add 35 to 40 cc. aq. reg. (1 part HNO_3 —2 parts HCl, 10 cc. for each 1 gr. metal), cover with clock-glass. After action, boil, transfer to porcelain, evap. in water bath; treat residue with conc. HCl and dilute, filter, add $BaCl_2$, stand 12 hours, filter, weigh. Wt. $BaSO_4 \times 13.724$ divided by wt. sample gives per cent. S.

1873—WILLIAMS, W. MATTIEU. *Chemical News*, Vol. 28, p. 266.

"The Estimation of Sulphur in Pig Irons."

NOTE.—"The 'simple and ready method' described in p. 248, *Chemical News*, by Mr. Piesse, is a very old one in common use in metallurgical laboratories, and described in rudimentary metallurgical treatises. The result obtained is somewhat below the truth, as some of the sulphur may escape oxidation, and pass off in combination with the hydrogen evolved. I have found that nitric acid, sp. gr. 1.2, is more convenient as a solvent than aqua regia; though liable to the same objection the loss of sulphur is less variable than when the aqua regia is used."

- 1873—PIESSE, CHARLES H. *Chemical News*, Vol. 28, p. 276.
"The Estimation of Sulphur in Pig Iron."

NOTE.—"In the explanation of the 'simple and ready' method described by me in the *Chemical News*, Vol. 28, p. 248, I do not perceive any claim to absolute originality; but that it was worthy of note is proved by the fact that it found place in the columns of the *Chemical News*. Persons using chemical processes by rule-of-thumb, as is generally the case in metallurgical laboratories, probably do not test the purity of their reagents, from whence, doubtless, arises the discordance of their results."

- 1873—KOPPMAYER, M. *Dingl. Polyt. J.*, Vol. 210, pp. 184-187.
"Bestimmung des Schwefels im Roheisen, Schmiedeeisen und Stahl."

Also in: *J. Chem. Soc. Lond.*, Vol. 27, p. 496 (1874).

Chemical News, Vol. 29, p. 134 (1874).

Bull. Soc. Chim. Paris, Vol. 21, p. 21 (1874).

Central Blatt, (1873), p. 790.

Ten grs. sample, pulverized in steel mortar, put in $\frac{1}{2}$ to $\frac{3}{4}$ liter flask. Three-hole stopper provides for hydrogen inlet, funnel and outlet to iodine in KI sol. which is in series of bulbs up an incline. After evol. with HCl excess iodine is titrated with hypo.

- 1874—ALLEN, ALFRED H. *Chemical News*, Vol. 29, p. 91. "Estimation of Silicon and Graphite in Pig-Irons."

Says that following Piesse's method gives too low results. Twelve hours is too short for pptn. and HCl, as recommended, will prevent full pptn. Should neutralize as completely as possible and let stand 24 to 36 hours or more BaSO₄ will come down.

- 1874—PIESSE, C. H. *Chemical News*, Vol. 29, p. 112. "Estimation of Carbon and Silicon in Pig-Irons."

States that to neutralize solution as Allen suggests would not appreciably hasten pptn. of BaSO₄.

1874—DROWN, TH. M. *Trans. Am. Inst. Min. Engrs.*, Vol. 2, p. 224. "Determination of Sulphur in Pig-Iron and Steel."

Also in: *Chemical News*, Vol. 29, p. 201.

Central Blatt, (1874), 362.

Evol. method absorbing H_2S in KMnO_4 soln., 1 gr. in 200 cc. of water. Uses 3 bottles or tubes in series for complete absorption.

	Silver soln		MMnO_4 soln
1	0.100	4	0.093
2	0.093	5	0.098
3	0.099	6	0.091

Purifies BaSO_4 above with soda fusion:

1	0.0900	4	0.0880
2	0.0890	5	0.0920
3	0.0920	6	0.0850
Mean		Mean	
0.0903		0.0883	

1874—FRESENIUS, R. *Ztschr. anal. Chem.*, Vol. 13, pp. 37-40. "Zur Bestimmung des Schwefels in Roheisen, Stahl, u. s. w."

Also in: *J. Chem. Soc. Lond.*, Vol. 27, p. 919 (1874).

Central Blatt, (1874), p. 362.

Jahresbericht, (1874), p. 967.

Evolution method with HCl absorbing in alk. lead soln., H_2 ats.; PbS oxidized with alk. fusion or Br .

Absorbent	Grs. sample	Grs. BaSO_4	% S
Br. soln.	10.652	0.0938	0.1209
Br. soln.	9.9937	0.0922	0.126
Alk. Pb. soln.....	9.9614	0.0879	0.121

1875—BOUSSINGAULT. *Ann. Chim. Phys.*, Series 5, Vol. 5, p. 145. "Etudes sur la transformation du fer en acier par la céméntation."

Also in: *Pol. J.*, Vol. 222, p. 447.

Central Blatt, (1877), p. 9.

Jahresbericht, (1876), p. 975.

Pages 174 to 177 on detn. of S: others use CuCl_2 , or Pb soln. B. prefers AgNO_3 ; dissolves in H_2SO_4 and weighs metallic Ag in Pt. 108 grs. Ag represents 16 grs. S. A sample of Swedish iron has 0.055 per cent. S., a white iron from Ria has 0.10 per cent. S. Uses very long necked flask; rubber connections.

1876—WAGNER, RUDOLF. *Ding. Polyt. J.*, Vol. 219, p. 544. "Ueber die Verwendbarkeit des Broms in der Hydrometallurgie, der Probirkunst und der chemischen Technologie."

Says Berthier dissolved iron samples in Br water for C and Si (*Annales des Mines*, 3, 209 and 215 (1833)) determinations; used by Nicklès and used by Fresenius (for use by two latter see prev. refs.).

1877—HIBSCH, J. EMANUEL. *Dingl. Polyt. J.*, Vol. 225, pp. 61-64. "Ueber einige Methoden zur Bestimmung des Schwefels im Roheisen."

Also in: *J. Chem. Soc. Lond.*, Vol. 32, p. 799 (1877).

Ztschr. anal. Chem., Vol. 18, p. 625 (1877).

Central Blatt, (1877), p. 602.

Jahresbericht, (1877), p. 1055.

Reviews methods:

1. Technical method—Gintl's FeCl_3 soln.
2. Exact detn.—Fresenius' with Weselsky's fusion modification.
3. Commercial—Cl over heated iron, SCl_2 into HCl and H_2SO_4 detd. grav.

	Koppmeyer's method	Fresenius' method	Gintl's method	Cl method
White pig	0.749	0.652	0.509	—
	0.682	0.535	—	—
	0.715 = av.	0.593 = av.	0.509 = av.	—
Gray pig	0.127	0.102	—	—
	0.121	0.098	—	—
	0.124 = av.	0.100 = av.	—	—
White pig	—	0.466	—	0.526

1879—ROLLET, A. *Dingl. Polyt. J.*, Vol. 233, p. 124. "Bestimmung des Schwefels in den Producten der Eisen-Industrie, den Erzen und den Brennmateriellen."

Also in: *J. Am. Chem. Soc.*, Vol. 1, p. 560 (1879).

J. Chem. Soc. Lond., Vol. 36, p. 976 (1879).

Ztschr. anal. Chem., Vol. 21, p. 122 (1882).

J. I. S. I., (1880), p. 359.

Central Blatt, (1879), p. 685.

Jahresbericht, (1879), p. 1031.

Declares the old process of dissolving in HNO_3 and pptg. with BaCl_2 is entirely untrustworthy; results neither absolutely nor relatively correct.

Very finely powdered (900 meshes per sq. cm.) iron or steel is taken in 2 to 4 gram portions in porcelain boat in tube at red heat and H_2 and CO_2 passed over and then through AgNO_3 soln. AgS is filtered, dried and weighed on tared paper. Prefers to burn AgS in boat and weigh Ag . 2 to 2.5 hours required; if substance cakes mix with S-free clay.

1881—SLOANE, T. O'CONNOR. *J. Am. Chem. Soc.*, Vol. 3, p. 37. "Note on the Precipitation and Purification of Barium Sulphate."

Iron always comes down.

Boiling with dil. HCl gives loss as BaS ; boiling with conc. H_2SO_4 makes results high as Ba in BaCl_2 goes to BaSO_4 ; fusions are troublesome.

S. precipitates in barely acid sol. and boils ppt. with conc. HCl for 1 min.; gets white BaSO_4 .

1882—EMMERTON, F. A. *Trans. Am. Inst. Min. Engrs.*, Vol. 12, p. 200. About methods of analysis of steel in lab. of Joliet Steel Co.

Uses Elliott's method, *Chem. News*, 23, 61. 5 grs. sample, 80 cc. 1 to 2 HCl , into NaOH soln. iodine end.

Sample	Elliott's iodine method	Fresenius' bromide method
1	0.309% S	0.296% S
2	0.089	0.091
3	0.070	0.074
4	0.008	0.007

1882—ZIEGLER. *J. I. S. I.*, (1882), p. 384. "Filtration of Barium Sulphate." Reported from *Chem. Zeitg.*, Vol. 5, p. 53, but not there.

Adds AgNO_3 after BaCl_2 to facilitate and bring down all BaSO_4 ; AgCl washed from ppt. with NH_4OH .

1882—TAMM, A. *Jernt-Kont. Ann.*, Vol. 37, p. 94-147. "Om dels methoder för framställande af bly, silfver, guld, koppar och zink, samt dels sätt att kemish undersöka jern och jernmalmer." Pages 137-140 on S.

Also in: *Berg. H. Zeit.*, Vol. 41, p. 448.

J. Chem. Soc. Lond., Vol. 44, p. 511 (1883).

Central Blatt, (1882), p. 766.

Reviews methods, especially evolution. Proposes to ignite the evolved gas in hydrogen and carbon dioxide before passing into silver nitrate solution.

1882—CRAIG, GEORGE. *Chemical News*, Vol. 46, p. 199. "Estimation of Sulphur in Iron and Steel." Ditto, p. 272, reply to Rocholl.

Also in: *J. Chem. Soc. Lond.*, Vol. 44, p. 121 (1883).

Ztschr. anal. Chem., Vol. 25, p. 259 (1886).

Central Blatt, (1883), p. 355.

Jahresbricht, (1882), p. 1266.

Berichte, (1882), p. 2927.

Results invariably higher than oxidation method by passing evolved H_2S into amm. H_2O_2 and weighing BaSO_4 . A sample giving 0.0302 per cent. S by KClO_3 and HCl gave 0.0357 per cent. S by peroxide method.

Replying to Rocholl:

			S in residue	
			liquid	solid
1	Cu in pig	% S	nil	nil
2	0.50%	0.063	nil	0.002
3	0.50	0.065	nil	0.003
	0.50	0.064	nil	

1882—ROCHOLL, H. *Chemical News*, Vol. 46, p. 236. "Estimation of Sulphur in Pig Iron."

Also in: *J. Chem. Soc. Lond.*, Vol. 44, p. 512 (1883).

Ztschr. anal. Chem., Vol. 25, p. 260 (1886).

Berichte, Vol. 16, p. 261.

Attacks Craig's statements as follows:

	Copper	Total S	S evolved	S in residue	% low
1	0.00%	0.075%	0.069%	0.006%	8
2	0.02	0.045	0.041	0.004	9
3	0.02	0.026	0.021	0.005	19
4	0.20	0.065	0.050	0.015	23
5	0.23	0.017	0.011	0.006	35
6	0.26	0.061	0.029	0.032	52
7	0.26	0.064	0.027	0.037	58
8	0.26	0.026	0.009	0.017	65
9	0.27	0.041	0.026	0.015	36
10	1.09	0.071	0.046	0.025	35

However, he does not answer Craig's rejoinder!

1883—CLASSEN, A., and BAUER, O. *Berichte*, Vol. 16, p. 1061. "Ueber die Anwendbarkeit des Wasserstoffsperoxyds in der Analytischen Chemie."

Also in: *Chemical News*, Vol. 47, p. 288 (1883).

To determine S in pig iron C. and B. use both Br in HCl and H_2O_2 in NH_3 , Na_2CO_3 or NaOH solution. Cut of rather cumbersome apparatus is main feature of detn. of S in iron portion of article. Apparatus has rubber connections.

1884—BAYLEY, THOMAS. "The Assay and Analysis of Iron and Steel, Iron Ores, and Fuel." E. and F. N. Spon, London.

For S in iron and steel gives oxidation method with Na_2CO_3 fusion to purify BaSO_4 . Few lines, only, pages 22-24.

1884—BRAND, ALBANO. *Berg. u. Hütten. Zeit.*, Vol. 43, p. 346. "Verfahren zur Analyse von Stahl."

Also in: *J. I. S. I.*, (1884), p. 660.

Central Blatt, (1884), p. 849.

Dissolves 10 grams metal in HCl, absorbs H_2S in burette filled with glass beads moistened with Br water; evaporates, filters, and ppts. $BaSO_4$. 1 paragraph only.

1884—PERILLON. *Bull. Soc. de l'ind. Miner*, Vol. 13, p. 103.
"Dosage rapide du Carbon, du Phosphorè, etc."

Also in: *Berg. u. Hütten. Zeit.*, Vol. 45, pp. 6-8, 20-22, 30-32.

Ztschr. anal. Chem., Vol. 32, p. 505 (1886).

Central Blatt, (1886), p. 203.

Berichte, Vol. 19, p. 3181 (1886).

Boussingault's method with new end point. Dissolves in 1-5 H_2SO_4 absorbing in $AgNO_3$; AgS washed, dissolved in HNO_3 , adds ferric nitrate and titrates to red with KSCN.

1884—SCHEURER-KESTENER. *Compt. rend.*, Vol. 99, pp. 876-877.
"Réaction de l'oxyde ferrique, à haute température sur quelques sulfates."

Also in: *J. Soc. Chem. Ind.*, (1885), p. 281.

SO_3 is given off when Fe_2O_3 is heated with $CaSO_4$, $MgSO_4$ and $PbSO_4$; does not occur with $BaSO_4$.

1884—TROILIUS, MAGNUS. *Trans. Am. Inst. Min. Engrs.*, Vol. 12, p. 507. "Sulphur Determination in Steel."

Evolution method: Boils 10 grs. sample in flask with 100 cc. water to expel air, then adds 100 cc. conc. HCl; absorbs in Br in HCl, sp. gr. 1.12; $BaSO_4$ ignited and weighed. Says usual $BaSO_4$ is contam. with SiO_2 . A steel with 0.30 per cent. Cu gives 0.16 per cent. S by Br and 0.16 per cent. by aq. reg. methods. Connections are of rubber.

1885—OSMOND, M. *Bull. Soc. Chim. Paris*, Vol. 43, p. 70. "Sur l'absorption et le dosage de petites quantitiés d'hydrogène sulfuré dans les mélanges gazeux."

Also in: *Ztschr. anal. Chem.*, Vol. 26, p. 239 (1887).

Chemical News, Vol. 57, p. 142 (1888).

Cannot use lead or copper salts to absorb H_2S because precipitation spreads along several bulbs and is not localized in first one.

1885—PETERS, J. *Bull. Soc. Chim. Paris*, Vol. 44, pp. 16-17.
"Dosage du Soufre dans les Aciers, Fers et Fontes."

Also in: *J. Chem. Soc. Lond.*, Vol. 48, p. 1161 (1885).

Ztschr. anal. Chem., Vol. 32, p. 506 (1885).

J. I. S. I., (1885), p. 618.

Chem. Zeit., Vol. 9, p. 1502 (1885).

Central Blatt, (1885), p. 691.

Jahresbericht, (1885), p. 1906.

Berichte, Vol. 18, p. 514 (1885).

10 grs. powdered sample is dissolved in 1-1 HCl, first cold, then boiling; H_2S caught in $KMnO_4$ soln. containing 50 to 60 grs. per l. to avoid loss with more dil. soln. Excess $KMnO_4$ decomposed with HCl, dilute, ppt. with $BaCl_2$ and weigh as usual. For irons with over 2 per cent. S use 5 or 2 grs. for analysis and add little conc. soda soln. to $KMnO_4$.

1885—REINHARDT. *Stahl u. Eisen*, Vol. 5, pp. 550-552. "Über Schwefelbestimmungs-Apparate."

Also in: *J. I. S. I.*, (1885), p. 650.

Mainly for sulfids with several per cent. of S which may be deposited in nooks of apparatus, thus escaping oxid. with Br. He uses Ledebur app. (see Ledebur, "Leitfaden f. Eisenhütten," 1880) or a flat flask; KOH may be put in first and $KMnO_4$ in a second. Br. in HCl is added to KOH soln. to oxidize H_2S to H_2SO_4 . Alk. plumbic oxide also makes good absorbent. App. illust. with 5 figs.

1885—RINMAN, L. *Jern-Kontorets Annaler*, Vol. 40, p. 362.
"Svafvel-prof pa tackjern."

Also in: *Berg. u. Hütt. Ztg.*, Vol. 45, p. 79 (1886).

Ztschr. anal. Chem., Vol. 32, p. 507 (1885).

J. I. S. I., (1886), p. 397.

Central Blatt, (1886), p. 218.

Jahresbericht, (1886), p. 1912.

R. found a mottled iron gave only 0.03 per cent. S by color. test but after remelting to gray iron got 0.075 per cent. S. Remelting sample is simplest and most trustworthy method.

1886—BRUGMAN, W. F. *School of Mines Quart.*, Vol. 8, p. 74.
"Influence of Copper on the Estimation of Sulphur."

Also in: *J. Anal. App. Chem.*, (1887), p. 97.

J. Chem. Soc. Lond., Vol. 52, p. 296.

J. I. S. I., (1887), p. 471.

Ztschr. anal. Chem., Vol. 27, p. 506 (1887).

Chemical News, Vol. 54, p. 290 (1886).

Central Blatt, (1887), p. 95.

Demonstrates that Cu does not interfere with evolution method.

Pig iron.....(0.835% Cu) by aq. reg.	0.228% S
fusion	0.226
evolution	0.228
Pig iron	0.025
Same after adding Cu.....	0.023
Steel, containing Cu	0.086
Same after adding more Cu.....	0.087
Steel, Cu-free	0.046
Same after adding Cu.....	0.048

No S can be detected in solution after boiling off the H_2S .

1886—SPRENGER. *Berg. u. Hütt. Ztg.*, Vol. 45, p. 471. "Verfahren zur Analyse von Eisen und Stahl."

Also in: *Ztschr. anal. Chem.*, Vol. 33, p. 503.

As aq. reg. method fails to get all S uses evolution method with special trap holding alcohol to retain Br which oxidizes S to H_2SO_4 . CO_2 generator is connected with apparatus. 1 or 2 gr. sample is used.

- 1886—MÖLLER, GUSTAV. *Berg. u. Hütt. Ztg.*, Vol. 45, pp. 198-199. "Ueber die Eggertz'sche Methode zur Bestimmung des Schwefels in Eisen."

Also in: *Stahl u. Eisen*, Vol. 6, pp. 581-589 (1886).

J. I. S. I., (1886), p. 1022.

J. Chem. Soc. Lond., (1887), p. 296.

Ztschr. anal. Chem., Vol. 32, p. 507.

Central Blatt, (1886), p. 489.

Berichte, Vol. 19, Part 3, p. 465 (1886).

Severely criticises Eggertz' method saying samples containing from 0.013 per cent. to 0.115 per cent. S all give same color. Also, from 16 to 80 per cent. of the sample dissolves in the allotted 15 mins., as the rate of soln. is due to per cent. carbon. The method is absolutely useless. (Thesis at Kgl. Bergakademie zu Berlin under H. Weding.)

- 1886—EGGERTZ, V. *Berg. u. Hütt. Ztg.*, Vol. 45, p. 545. "Ueber die Colorimetrische Bestimmung des Schwefels im Eisen."

Also in: *Central Blatt*, (1887), p. 95.

Berichte, Vol. 20, Part 3, p. 76 (1887).

Reply to G. Möller's attack. Sample must be finely (to pass 0.5 mm. holes) powdered.

- 1886—WIBORGH, J. *Jern-Kont. Annaler*, Vol. 41, pp. 105-119. "Nytt Kolorimetrisk svafvelprof för jern."

Also in: *Stahl u. Eisen*, Vol. 6, p. 230 (1886).

Berg. u. Hütt. Ztg., Vol. 45, p. 112 and p. 123.

Chemical News, Vol. 54, p. 158 (1886).

Ztschr. anal. Chem., Vol. 32, p. 504.

J. Anal. App. Chem., Vol. 1, p. 98 (1887).

J. I. S. I., (1886), p. 396.

Dingl. Poly. J., Vol. 260, p. 179.

J. Chem. Soc. Lond., Vol. 50, p. 743 (1886).

Central Blatt, (1886), p. 329.

Berichte, Vol. 19, Part 3, p. 364 (1886).

Colorimetric method with apparatus and color standards. Cloth over top of apparatus has been treated with $\text{Cd}(\text{OAc})_2$ soln. (5 grs. in 100 cc. H_2O). The flask is half filled with water, the cloth is stretched and the water boiled; the metal is lowered in its little tube; 10 cc. dil. H_2SO_4 for each 0.4 gr. sample then added and boiled for 10 mins. after complete solution. Method is rapid and accurate with Cu and As offering no interference.

Wiborgh's	BaCl_2	Wiborgh's	BaCl_2
0.005	0.005	0.028	0.029
0.005	0.006	0.039	0.038
0.007	0.008	0.04	0.037
0.0075	0.005	0.05	0.047
0.0075	0.005	0.06	0.061
0.012	0.01	0.07	0.068
0.012	0.014	0.1	0.093
0.015	0.013	0.135	0.134
0.018	0.018	0.15	0.145
0.02	0.025	0.21	0.19
0.02	0.02	0.35	0.34
0.023	0.024	0.45	0.46
0.023	0.024	0.7	0.66
0.025	0.022		

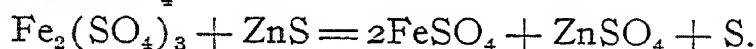
1887—FÖHR. *Chem. Tech. Zeit.* (Öest.), p. 105.

Also in: *Ztschr. Chem. Ind.*, Vol. 1, p. 314 (1887).

Central Blatt, Vol. 58, p. 871 (1887).

Jahresbericht, (1887), p. 2398.

Dissolves sample in dil. H_2SO_4 , leads H_2S into amm. Zn soln.; treats the ZnS with $\text{Fe}_2(\text{SO}_4)_3$ and titrates directly with KMnO_4 .



1887—MORGAN, J. JAS. *Industrial Review*. Copied into *Chemical News*, Vol. 56, p. 82 (1887). "Rapid Methods for the Determination of Silicon, Sulphur and Manganese in Iron and Steel."

Also in: *J. Chem. Soc. Lond.*, Vol. 52, p. 1140 (1887).

J. Anal. App. Chem., Vol. 1, p. 418 (1887).

Ztschr. anal. Chem., Vol. 32, p. 507.

Central Blatt, (1887), p. 1268.

Jahresbericht, (1887), p. 2427.

Berichte, Vol. 20, Part 3, p. 742 (1887).

Parry's method as used at Ebbw Vale Iron Co.

Treats 0.5 gr. sample in flask with 60 cc. dil. H_2SO_4 and H_2S is absorbed in 50 cc. $\text{Pb}(\text{OAc})_2$ soln. (0.2 gr. salt in 1 l.). Results may agree to 0.01 per cent. with oxid. method. Apparatus is side-arm flask provided with trapped thistle tube. Side arm dips into tall beaker or tube holding Pb soln.

1887—PLATZ, B. *Stahl u. Eisen*, Vol. 7, p. 256. "Zur Bestimmung des Schwefels im Eisen."

Also in: *J. Chem. Soc. Lond.*, Vol. 52, p. 1141 (1887).

J. I. S. I., (1887), Part 1, p. 471.

Central Blatt, (1887), p. 579.

Jahresbericht, (1887), Part 2, p. 2398.

Five grs. sample is dissolved in 1.185 HNO_3 and evap. to dryness. Takes up in HCl , dilutes and ppts. with BaCl_2 , cold, stand 12 hrs. Burns paper wet at low temp. and then ignites strongly to oxid. BaS . Only 5 to 10 per cent. Fe_2O_3 with BaSO_4 by this procedure which is neglig. with small per cent. S; for mush S purify BaSO_4 with conc. HCl , dilute, add BaCl_2 , boil, filter and ignite.

Tests:

Taken	Found
7.143 grs. Fe_2O_3 (5 grs. Fe)	0.4120 gr. BaSO_4 = 1.132% S
+ 25 cc. Na_2SO_4 to equal	0.4105 gr. BaSO_4 = 1.127
0.4070 gr. BaSO_4 or 1.118% S	0.4098 gr. BaSO_4 = 1.126
7.143 grs. Fe_2O_3	0.0447 gr. BaSO_4 = 0.123% S
+ Na_2SO_4 to equal	0.0460 gr. BaSO_4 = 0.126
0.0440 gr. BaSO_4 or 0.120% S	0.0443 gr. BaSO_4 = 0.122
	0.0450 gr. BaSO_4 = 0.124
7.143 grs. Fe_2O_3	0.0040 gr. BaSO_4 = 0.0110% S
+ Na_2SO_4 to equal	0.0042 gr. BaSO_4 = 0.0115
0.0040 gr. BaSO_4 or 0.0110% S	0.0040 gr. BaSO_4 = 0.0110
	0.0039 gr. BaSO_4 = 0.0107

1887—TAMM, ADOLF. *Jern-Kont. Annaler*, Vol. 42, p. 4. "Nagra meddelander rörande kennisk profning af jern och jernmaler."

Also in: *Stahl u. Eisen*, Vol. 7, p. 627 (1887).

J. Anal. App. Chem., (1888), p. 109.

Ztschr. anal. Chem., Vol. 32, p. 508.

J. I. S. I., (1887), Part 2, p. 369.

Berg. u. Hutt. Ztg., Vol. 46, p. 238 and Vol. 47, p. 148.

Central Blatt, (1887), p. 876 and 1362.

Jahresbericht, (1887), Part 2, p. 2405.

Purifies BaSO_4 ppt. with conc. HCl and Na_2CO_3 fusion. Finds 0.0025 gr. BaSO_4 left in FeCl_3 soln. Wiborgh's colorimetric method good for small amounts of S, but accuracy diminishing as S increases; it is more accurate than silver foil method commonly used in Sweden.

1888—ARNOLD, J. O., AND HARDY, HENRY J. *Chemical News*, Vol. 58, p. 41 and p. 70. "New Methods for the Estimation of Sulphur in Steel and Steel-Making Iron," and "Estimation of Sulphur in Iron and Steel."

Also in: *J. Chem. Soc. Lond.*, Vol. 54, p. 1333 (1888).

J. Am. Chem. Soc., Vol. 10, p. 84 (1888).

J. Anal. App. Chem., Vol. 2, p. 425 (1888).

Ztschr. anal. Chem., (1888), p. 1143.

Ztschr. angew. Chem., (1888), p. 494.

Central Blatt (1888), p. 1183.

Jahresbericht, (1888), p. 2529.

Berichte, (1888), p. 855.

Review volumetric, colorimetric and oxidation methods. Use dil. H_2SO_4 with current of hydrogen to evolve H_2S from sample absorbing in a series of tubes containing $\text{Pb}(\text{OAc})_2$ soln.; each tube colored represents 0.01 per cent. S in sample. Cu does not interfere. Rubber connections.

In second article replies to Morgan upholding accuracy and new speed obtainable with his modifications of color. and evol. methods.

	BaSO_4		New apparatus evol. meth.
Steel	0.07% S		0.06% S (seven times)
Iron	0.12		0.11
Steel	0.01		0.01 (four times)

- 1888—MORGAN, J. J. *Chemical News*, Vol. 58, p. 59 and p. 63.
“On the Colorimetric Determination of Sulphur in Iron and Steel,” and “On the Determination of Sulphur in Iron and Steel.”

Also in: *J. Chem. Soc. Lond.*, (1888), p. 1334.

Central Blatt, (1888), p. 1184.

Jahresbericht, (1888), p. 2530.

Berichte, (1888), p. 856.

Disparages Arnold and Hardy's new method and upholds Parry's method which is considered only a modification of Frankland's method for lead in water, it is not a new process, at all.

“We may here remark that the non-uniformity in composition of the steel employed as a “standard” is felt in a more marked degree than in the colorimetric determination of combined carbon.”

Regarding grav. oxid. method says $\text{Ba}(\text{NO}_3)_2$ can be removed by evap. or washings; that amt. of acid will make results high or low; that is a tedious process; that BaSO_4 is soluble in FeCl_3 soln. Results are accurate and concordant, however.

- 1888—GRÖNDAHL, VICTOR. *Chem. Tech. Zeitung*, Vol. 6, p. 621.

Also in: *Central Blatt*, (1888), p. 1398.

Jahresbericht, (1888), p. 2529.

“Schwefel Bestimmung in Eisen und Stahl mit H_2O_2 .”

Apparently nothing new over previous evol. method which oxidizes H_2S to H_2SO_4 with H_2O_2 .

- 1888—REIS, M. A. VON. *Stahl u. Eisen*, Vol. 8, pp. 827-831. “Zur Bestimmung des Phosphors und Schwefels im Eisen.”

Also in: *Zeit. f. anal. Chem.*, Vol. 32, p. 504.

J. Chem. Soc. Lond., Vol. 56, p. 648 (1889).

Central Blatt, (1889), p. 115.

Jahresbericht, (1889), p. 2342.

Says S escapes as S and H_2S during solution of iron in HNO_3 ; criticises procedure of Platz and of Tamm.

Recommends heating 5 grs. of sample with 5 grs. of mixture of 2 parts MgO and 1 part Na_2CO_3 in a platinum dish at bright redness for 10 mins. The cake is broken and again heated for 20 mins. Finally ppts. as BaSO_4 . One analysis requires 6 hours and an analyst can do 6 samples a day.

Analyses as by Meineke, are given and following:

Sample	Peroxide evolution method	Residual		Total	MgO method	% loss by evol. method	
		Solution	Precipit				
1	Gray pig	0.035	0.003	0.005	0.043	0.039	0.008
2		0.030	0.002	0.008	0.040	0.043	0.010
3		0.033	0.004	0.004	0.041	0.039	0.008
4	White pig	0.032	0.002	0.005	0.039	0.040	0.007
5		0.050	0.002	0.005	0.057	0.059	0.007
6		0.053	0.006	0.010	0.069	0.067	0.016
7		0.071	0.002	0.005	0.078	0.080	0.007
8		0.072	0.003	0.010	0.085	0.080	0.013
9		0.090	0.006	0.008	0.104	0.100	0.014
10		0.107	0.006	0.010	0.123	0.130	0.016
11		0.181	0.006	0.020	0.207	0.200	0.026
12		0.252	0.010	0.015	0.277	0.280	0.025
13		0.531	0.009	0.010	0.550	0.540	0.008
14	Flusseisen	0.044	0.000	0.008	0.052	0.054	0.008
15		0.088	0.000	0.007	0.095	—	0.007
16		0.029	0.000	0.008	0.037	—	0.008
17	Siegener pig	0.014	0.000	0.015	0.029	0.030	0.015
18		0.070	0.000	0.025	0.095	0.093	0.025

1888—KONINCK, L. L. DE. *Ztschr. für angew. Chem.*, Vol. I, p. 311. "Bestimmung des Schwefels im Eisen und in den von Salz und Schwefelsäure zersetzbaren Schwefelmetallen."

Also in: *J. Soc. Chem. Ind.*, Vol. 7, p. 525 (1888).

Revue des Mines, (1888), p. 3.

Chemical News, Vol. 58, p. 208 (1888).

J. Anal. App. Chem., Vol. 2, p. 424 (1888).

J. Chem. Soc. Lond., Vol. 56, p. 437 (1889).

Ztschr. anal. Chem., Vol. 31, p. 705 (1892).

Central Blatt, (1888), p. 1040.

Jahresbericht, (1888), p. 2529.

Berichte, (1888), p. 2529.

The method of 1870 is modified by using $\text{Hg}(\text{CN})_2$ and NH_4Cl to avoid colloidal HgS and washing out the AgBr .

1888—LUCION, MARCEL. *Chem. Ztg.*, Vol. 12, p. 427. "Ueber die Fällung von Baryumsulfat in bromhaltigen Flüssigkeiten."

Br in the soln. is without influence on the solubility of BaSO_4 .

Direct pptn.	0.8542 gr. BaSO_4
Br. removed	0.8541 gr. BaSO_4

1888—LUETSCHER, J. *The Iron Age*, Vol. 41, p. 325. "The Use of Centrifugal Machines in the Iron and Steel Laboratory."
Also in: *J. I. S. I.*, (1888), p. 379.

H_2S is absorbed in Pb soln. and the PbS read off in a grad. tube after whirling in centrif. machine. Accurate to 0.003 per cent. S.

Uses dilute acid and rubber connections.

1888—MEINEKE, C. *Zeit. f. angew. Chem.*, Vol. 1, p. 376-380. "Über die Bestimmung des Schwefels im Eisen."

Also in: *Ztschr. anal. Chem.*, Vol. 32, p. 508 (1888).

J. Soc. Chem. Ind., Vol. 7, p. 645 (1888).

J. Anal. App. Chem., (1889), p. 89.

Chemical News, Vol. 59, p. 107 (1889).

Vers. d. Ges. f. Angew. Chemie-P. Ztg., Vol. 33, p. 311 (1888).

Central Blatt, (1888), p. 912.

Jahresbericht, (1889), p. 2525.

Berichte, Vol. 26, p. 161 (1893).

Uses peroxide evolution method and CuCl_2 grav. method.

Material	Evolution	Residue	% in residue
Spiegel	0.00 % S	0.030% S	100
	0.004	—	—
Siegerländer pig.....	0.022	0.025	52
	0.023	0.028	55
	0.022	—	—
White Swedish iron...	0.037	0.016	30
Thuringes pig.....	0.062	0.010	14
	0.065	0.014	17
Gray Thomas pig.....	0.114	0.069	37
	0.122	0.056	31
White Thomas pig.....	0.504	0.008	1.5
	0.519	0.008	1.5
	0.599	0.00	00

	Evolved and in residue	CuCl ₂ method
Spiegel	0.030	0.029
	0.047–0.051	0.052
Pig	0.053	0.059
Basic pig	0.079	0.088–0.087
Gray pig	0.181–0.183	0.169
White pig	0.512–0.523	0.509–0.507
	0.599	0.604

1888—PROST, EUG. *Bull. acad. roy. Belg.*, Vol. 16, p. 216.
 “Étude de l'action de l'acide chlorhydrique sur la fonte.”

Also in: *J. I. S. I.*, (1889), p. 390.

Some organic S cpds. evolved and some remain in residue.

1888—THÖRNER, WIL. *Ztschr. angew. Chem.*, Vol. 1, p. 487.
 “Über einen verbesserten Zersetzungs- und Absorptions-Apparat.”

Also in: *Ztschr. anal. Chem.*, Vol. 33, p. 690.

Evolution apparatus with condenser and special absorption tube. No rubber in connections.

1888—WINDER, B. W. *Chemical News*, Vol. 58, p. 95. “Estimation of Sulphur in Iron and Steel.”

Uses Arnold and Hardy's method with good and quick results; precautions as to reagents, air in apparatus. All acids contain S.

1889—JANNASCH AND RICHARDS. *J. Prakt. Chem.*, N. S. Vol. 39, pp. 321–334. “Ueber die Bestimmung der Schwefelsäure bei Gegenwart von Eisen.”

Also in: *Chemical News*, Vol. 60, p. 19 (1889).

Cold ferric solutions do not dissolve BaSO₄; iron not removed from BaSO₄ with HCl; the Ba-Fe sulfate is decomposed only at red heat. Many other valuable experiments but more related to S in pyrites.

1889—MARSH, C. W. *Chemical News*, Vol. 59, p. 309. "The Reduction of Barium Sulphate to Barium Sulphide on Ignition with Filter Paper."

Finds BaS always present; burn in open and ignite after adding H_2SO_4 .

1889—PLATZ, B. *Stahl u. Eisen*, Vol. 9, p. 405. "Zur Bestimmung des Schwefels im Eisen."

Also in: *Central Blatt*, (1889), p. 831.

Jahresbericht, (1889), p. 2343.

Discussion with von Reis; no H_2S lost when iron is dissolved in HNO_3 although a trace noticed by smell.

Sample	HNO_3	Aq. Reg.	Platz
1	0.023	0.023	0.019
2	0.039	0.035	0.034
3	0.046	0.049	0.041
4	0.082	0.081	0.078
	0.082	0.082	—
5	0.109	0.105	0.103

1889—REIS, M. A. VON. *Stahl u. Eisen*, Vol. 9, p. 496-7. "Zur Bestimmung des Schwefels im Eisen."

Also in: *J. I. S. I.*, (1889), p. 479.

S is given off as H_2S when iron is dissolved in HNO_3 at a temp. as low as 60°C . Elemental S may be found on cover glass over a beaker.

1889—VOSMAER, A. *Chem. Ztg.*, Vol. 13, p. 695. "Ueber die Wiborghsche colorimetrische Schwefelbestimmungsmethode."

Also in: *Central Blatt*, (1889), p. 192.

Jahresbericht, (1889), p. 2333.

Omits sample tube in Wiborgh's method. Makes a "normal iron."

Classen's app.	Flask	Gravimetric
0.080% S	0.079% S	0.11% S
0.080	0.081	—

1890—COHEN, J. B. *J. S. C. I.*, Vol. 9, p. 16. "Wiborgh's Method for the Analysis of Sulphur in Iron and Steel."

Also in: *J. Anal. App. Chem.*, Vol. 4, p. 335.

J. Chem. Soc. Lond., Vol. 58, p. 1463 (1890).

Central Blatt, (1890), p. 542.

Jahresbericht, (1890), Part 2, p. 2393.

Simplified color. flask; uses 0.1 gr. to 0.8 gr. sample and 1-5 H_2SO_4 , boiling 10 min. after solution.

1890—REINHARDT, C. *Stahl u. Eisen*, Vol. 10, p. 430. "Schnelle gewichtsanalytische Schwefelbestimmung in Stahl und Roheisen."

Also in: *J. Chem. Soc. Lond.*, Vol. 58, p. 1464 (1890).

Ztschr. angew. Chem., (1890), p. 308.

Central Blatt, (1890), p. 79.

Jahresbericht, (1890), p. 2392.

NaOH to absorb H_2S contains known amt. of S to make larger ppt. of BaSO_4 when oxidized with Br. and weighed. Uses HCl, 1.19 sp. gr., and rubber stopper.

1890—ARCHBUTT, L. *J. Soc. Chem. Ind.*, Vol. 9, p. 25. "Determination of Sulphur in Iron and Steel."

Also in: *J. Chem. Soc. Lond.*, Vol. 58, p. 1463.

Ztschr. f. angew. Chem., (1890), p. 149.

Ztschr. f. anal. Chem., Vol. 32, p. 503.

Central Blatt, (1890), p. 543.

Jahresbericht, (1890), p. 2393.

Oxidation method dissolving in hot aq. reg. and KClO_3 , evaps. to dryness; ppts. in conc. sol. with BaCl_2 . Checks with evol. method so author concludes FeCl_3 does not dissolve BaSO_4 .

Volume	Wt. BaSO_4	% S		Neutral solution		Acid solution (5cc.)	
63 cc.	0.0455	0.125	1	0.0530	0.146%	0.0515	0.142%
250	0.0415	0.114	2	0.0414	0.114	0.0413	0.114
500	0.0330	0.091	3	0.0415	0.114	0.0415	0.114
750	0.0270	0.074	4	0.0337	0.093	0.0330	0.091
			5	0.0298	0.082	0.0315	0.087
70 cc.	0.0416	0.114	6	0.0245	0.067	0.0245	0.067
250	0.0386	0.106	7	0.0215	0.059	0.0205	0.056
500	0.0391	0.108					
750	0.0378	0.104					

- 1890—BLUM, L. *Zeit. anal. Chem.*, Vol. 29, p. 138. "Zur Bestimmung des Schwefels im Eisen."

Also in: *Ztschr. angew. Chem.*, (1890), p. 458.

J. Chem. Soc. Lond., Vol. 58, p. 921 (1890).

J. Soc. Chem. Ind., Vol. 9, p. 769 (1890).

Central Blatt, (1890), p. 976.

Jahresbericht, (1890), p. 2392.

Berichte, (1890), p. 411.

Discussion of methods with modification of Marcel Lucion's (1888) method—HBr must be neutralized before pptg. BaSO₄.

- 1890—THÖRNER, W. *Chem. Ztg.*, Vol. 14, p. 1655. "Mittheilungen aus der Laboratoriumspraxis."

Also in: *Ztschr. f. anal. Chem.*, Vol. 32, p. 506.

Central Blatt, (1891), p. 208.

Jahresbericht, (1890), p. 2600.

Berichte, (1891), p. 47.

Absorption tube for evolution method; consists of a long flat tube between bulbs.

- 1891—CAMP, J. M. *J. Anal. App. Chem.*, Vol. 5, p. 409. "Absorption Apparatus for Sulphur Determination."

Also in: *J. I. S. I.*, (1891), p. 326.

Upright absorption tube to hold glass beads and Br water; inlet for gas just above stopcock over tip at base.

- 1891—HATTENSAUR, G. *Chem. Ztg.*, Vol. 15, p. 521. "Zur Schwefelbestimmung in Eisen und Stahl."

Also in: *J. Soc. Chem. Ind.*, Vol. 10, p. 797 (1891).

Ztschr. anal. Chem., Vol. 32, p. 509.

J. S. C. I., (1891), p. 797.

J. I. S. I., (1891), p. 326.

Stahl u. Eisen, Vol. 8, p. 671 (1891).

Central Blatt, (1891), p. 995.

Jahresbericht, (1891), p. 2428.

Discussion of methods; evol. with oxid. by Br considered as good as Meinecke's CuCl_2 method. Additional note in *Stahl u. Eisen* says ev. method works on low Mn stock but not as well on spiegel and ferro Mn.

Stock	% evol. S	CuCl_2 method	% Cu
Martin steel	0.020	0.022	0.005
	0.063	0.062	0.004
	0.033	0.034	0.007
	0.007	0.008	0.024
	—	0.025	0.183
	0.027	0.027	0.160
	0.012	0.011	0.060

1891—REIS, VON, and WIGGERT, F. *Stahl u. Eisen*, Vol. 11, p. 480. "Zur Bestimmung von Schwefel im Eisen."

Also in: *J. Chem. Soc. Lond.*, Vol. 60, p. 1549 (1891).

Ztschr. angew. Chem., (1891), p. 457.

J. I. S. I., (1891), p. 325.

Central Blatt, (1891), p. 218.

Part I, by F. Wiggert about apparatus.

Part II, by von Reis on determinations.

Special apparatus for evol. method by usual reagents. Absorbs H_2S in ammon. H_2O_2 and by pptg. with $\text{Ba}(\text{NO}_3)_2$ is able to filter BaSO_4 in 15 mins. thus making detn. in 2 hours where usual German evol. method is said to require 12 hours. No rubber in connections.

Sample	Air removed from flask	Flask contains air
1	0.097% S	0.102% S
	0.101	0.102
2	0.105	0.106

Sample	Time for evolution	Gray iron	White iron	White iron
3	15 min.	0.035	0.110	0.189
	20	0.037	0.112	0.212
	25	0.035	0.116	0.216
	30	0.036	0.119	0.217
	35	0.036	0.116	0.223
	40	0.036	0.119	0.219
	45	0.037	0.118	0.224
	50	0.036	0.120	0.225

"The principle of the method depends on the fact that in a neutral, metal-free, boiling solution even very small amounts of sulfuric acid are precipitated rapidly in granular form by barium nitrate."

Gray iron			White iron		
5 grs. sample	10 grs. sample		5 grs. sample	10 grs. sample	
0.030 to 0.032	0.032 to 0.033		0.084 to 0.086	0.084 to 0.088	
0.046 to 0.050	0.050 to 0.050		0.066 to 0.070	0.072 to 0.076	
0.033 to 0.036	0.034 to 0.036		0.100 to 0.102	0.123 to 0.130	
0.068 to 0.074	0.070 to 0.074		0.125 to 0.127	0.123 to 0.130	
			0.048 to 0.048	0.048 to 0.050	
			0.085 to 0.088	0.085 to 0.090	

Pig iron			Pig iron		
BaSO ₄ weighed	BaSO ₄ measured	Grade	BaSO ₄ weighed	BaSO ₄ measured	Grade
0.155	0.152	38	0.059	0.048	12
0.150	0.144	36	0.088	0.076	19
0.076	0.072	18	0.230	0.210	52.5
0.078	0.076	19	0.227	0.206	51.5
0.072	0.080	20			
0.064	0.068	17			
0.052	0.060	15			
0.047	0.048	12			
0.092	0.092	23			
0.106	0.102	25.5			
0.090	0.086	22.5			
0.077	0.070	17.5			
0.058	0.060	15			
0.053	0.060	15			

Steel		
BaSO ₄ weighed	BaSO ₄ measured	Grade
0.044	0.042	10.5
0.047	0.044	12
0.056	0.056	14
0.049	0.050	12.5
0.058	0.056	14
0.039	0.042	10.5
0.050	0.044	11
0.032	0.030	7.5

1891—ROSSI, A. J. *Stahl u. Eisen*, Vol. 11, p. 927. "Analytische Methode. Bestimmung von Schwefel."

Also in: *Central Blatt*, (1892), p. 180.

Evolution method, oxidizing with Br in HCl soln. In France and Alsace-Lorraine the Br-HCl soln. is put in a porcelain crucible, Na₂CO₃ added, evap. to dryness, diss. in H₂O, add HCl and ppt. with BaCl₂.

1891—WEDDING, HERMANN. "Handbuch der Eisenhüttenkunde." F. Vieweg & Sohn, Braunschweig. P. 690, Schwefel.

Methods given: (1) Platz, 1887; (2) Gintl & Meinecke; (3) Eggertz; (4) Wiborgh; (5) Johnston's Br; (6) Drown's KMnO_4 ; (7) Craig's H_2O_2 ; (8) Berzelius' AgNO_3 ; (9) Dewery's weighing CdS ; (10) Weil & Elliott's NaOH and I; (11) Föhr's $\text{ZnS-FeSO}_4\text{-KMnO}_4$.

1891—WILSON, J. M. *J. Anal. App. Chem.*, Vol. 5, p. 439. "A Method of Standardizing Iodine Solution for the Determination of Sulphur in Steel and Pig Iron."

Also in: *Chemical News*, Vol. 64, p. 252.

J. Chem. Soc. Lond., Vol. 62, p. 382 (1892).

Ztschr. angew. Chem., (1891), p. 650.

Central Blatt, (1892), p. 142.

Jahresbericht, (1891), p. 2428.

Iodine solution is standardized against a sample containing known amount of sulfur.

Sample	Iodine	Br in HCl
Car 2238	0.067	0.063
2nd sample	0.060	0.064
Car 3614	0.069	0.072
	—	0.071
Car 4326	0.080	0.075
2nd sample	0.069	0.064
	—	0.063
Car 8113	0.073	0.068
	—	0.068

1892—BABBITT, H. C. *J. Anal. App. Chem.*, Vol. 6, p. 301. "Wiborgh's Colorimetric Sulfur Determination."

Also in: *J. I. S. I.*, Vol. 43, p. 408 (1893).

Ztschr. anorg. Chem., (1893), p. 395.

Central Blatt, (1892), p. 547.

Discusses processes and apparatus with cut of Wiborgh's; no data.

1892—CLYMER, LEE S. *J. Anal. App. Chem.*, Vol. 6, p. 318. "Sulphur Determinations by Different Methods."

Also in: *Ztschr. anorg. Chem.*, Vol. 3, p. 396 (1893).

J. I. S. I., Vol. 43, p. 408 (1893).

Central Blatt, (1892), p. 544.

Reviews and discusses methods; thinks errors in aq. reg. method due to manipulation. SiO_2 may separate and basic sulfate may come down in neutral solutions. Portions of the same lot sent to prominent labs. of U. S. and Germany gave low and high results by both evol. and oxid. methods:

0.005	0.011	0.013	0.013	0.019	0.024
0.008	0.012	0.013	0.015	0.020	
0.009	0.012	0.013	0.017	0.021	
0.010	0.012	0.013	0.017	0.022	

1892—EASTWICK, A. T. *J. Anal. App. Chem.*, Vol. 6, p. 246.
 "The Determination of Sulfur in Iron and Steel."

Also in: *Central Blatt*, (1892), p. 423.

Evolution method: 3 grs. sample, 80 cc. dil. HCl and rubber stopper and tubing connections with small between-flask to catch HCl. Declares method checks to 0.004 per cent. with other methods. Cut of app.

1892—WILLIAMS, F. H. *Eng. Soc. West. Penn.*, Vol. 8, p. 328.
 "Note on the use of Hot Acid in the Evolution of Sulphur as H_2S from Pig Iron."

Hot HCl always gives higher results than cold acid in evol. S detn. No S escapes first abs. bulb. Residues always contain S, less when hot acid is used.

Boiling			Cold—slow		
1	0.064	1	0.051
2	0.049	2	0.039
3	0.057	3	0.040
4	0.013	4	0.008
5	0.060	5	0.050
6	0.186	6	0.159
7	0.097	7	0.087
Conc. hot			Dil. hot		
0.049	0.050	0.051	0.044	Dil. cold	
			0.030 0.034		

1892—SCHNEIDER, A. *Ztschr. physikal. Chem.*, Vol. 10, p. 423.
 "Ueber einen Fall der festen Lösung."

Also in: *Chem. Ztg.*, Vol. 16, p. 326 (1892).
J. I. S. I., Vol. 43, p. 409 (1893).

Disputes Jannasch and Richards claims about iron going into BaSO_4 ppt. Claims they confused "solid solution" with "double sulphate." No matter how much iron is present about same enters ppt.; limits are 1.12 to 1.38 per cent., average, 1.24 per cent.

- 1892—LEEuwEN, J. VAN. *Rec. Trav. Chim. Pays-Bas.*, Vol. 11, p. 103. "L'influence du soufre du gaz de houille sur le dosage du soufre par fusion."

Also in: *Central Blatt*, Vol. 63, Part 2, p. 757 (1892).

Use alcohol or benzine flame to make sulfur fusions.

- 1892—PAYNE, H. L. *J. Anal. App. Chem.*, Vol. 6, p. 481. "Standard Iodine Solution: A Method for its Preparation."

Also in: *Ztschr. angew. Chem.*, Vol. 6, p. 117 (1893).

Chemical News, Vol. 66, p. 286.

J. I. S. I., Vol. 43, p. 409 (1893).

Ztschr. anorg. Chem., Vol. 4, p. 320 (1893).

J. Am. Chem. Soc., Vol. 16, p. 112 (1894).

Stahl u. Eisen, Vol. 13, p. 247.

Using Elliott's method standardizes iodine soln. by adding known amount of KMnO_4 to acid KI soln.

- 1892—RIPPER, M. *Ztschr. anorg. Chem.*, Vol. 2, p. 36. "Beitrage zur Gewichtsanalyse der Schwefelsäure."

Also in: *J. Chem. Soc. Lond.*, Vol. 64, p. 239 (1893).

Critical discussion. Sulphate reduced by filter paper is reoxidized and impurities removed with HCl and Br; results given.

- 1892—BLUM, L. *Ztschr. anal. Chem.*, Vol. 31, p. 290. "Absorptionsapparat zur Bestimmung des Schwefels im Eisen."

Also in: *J. Chem. Soc. Lond.*, Vol. 62, p. 1376 (1892).

J. Soc. Chem. Ind., Vol. 12, p. 63 (1893).

Stahl u. Eisen, Vol. 12, p. 801 (1892).

Ztschr. angew. Chem. (1892), p. 466.

Central Blatt, (1892), p. 423.

Berichte, (1892), p. 873.

A two-part absorption tower for evol. method.

- 1892—THÖRNER, W. *Stahl u. Eisen*, Vol. 12, p. 527. "Zur Bestimmung von Schwefel in Eisen und Stahl."

Also in: *Ztschr. anorg. Chem.*, (1892), p. 475.

Central Blatt, (1892), p. 131.

Same apparatus as presented previously in 1888 and 1890.

- 1893—M., E. *Stahl u. Eisen*, Vol. 13, p. 686. "Zur Schwefelbestimmung."

Also in: *Ztschr. angew. Chem.*, Vol. 6, p. 608 (1893).

Central Blatt, (1893), p. 623.

Uses Blum's (1892) apparatus slightly modified; upright tube is corrugated to promote absorption.

- 1893—CROBAUGH, F. L. *J. Anal. App. Chem.*, Vol. 7, p. 280. "Cadmium Chloride as an Absorbent of Hydrogen Sulfid."

Also in: *Ztschr. anal. Chem.*, Vol. 36, p. 791.

Evolution method dissolving in cold dil. HCl and titrating the H_2S absorbed in $CdCl_2$ soln. with iodine (1 cc. = 0.005 per cent. Fe). Uses minimum amount of Cd soln. and catches all H_2S in layer of liquid 2 inches deep.

- 1893—HOOPER, H. A. *Chemical News*, Vol. 68, p. 191. "A New Method for the Rapid Estimation of Sulphur in Steels, Pig Irons, etc."

Also in: *J. Chem. Soc. Lond.*, Vol. 66, Part 2, p. 67.

Ztschr. anorg. Chem., Vol. 6, p. 208.

Central Blatt, (1893), p. 1032.

Evolution method: dissolves in dil. HCl absorbing in NaOH and titrating with standard lead solution until a drop gives no further coloration. 1 cc. lead soln. = 0.0005 grs. S.

- 1893—MACKENZIE, J. KENNETH. *J. Anal. App. Chem.*, Vol. 7, p. 134. "Absorption Bulb for Sulfur Determinations."

Also in: *J. Soc. Chem. Ind.*, Vol. 12, p. 624 (1893).

Central Blatt, (1893), p. 956.

A three-compartment bulb with stop cock draining the central and lowest portion.

1893—PARRY AND MORGAN. *Industries*, Vol. 14, p. 330. "The Analysis of Iron and Steel."

Also in: *Chemical News*, Vol. 67, p. 247 (1893).

A. Aqua regia method—evaporate 3 or 4 times with HCl to expel HNO_3 , precip. in dil. soln. slightly acid with HCl since BaSO_4 is soluble in acid FeCl_3 . Iron coloring pink is disregarded but red BaSO_4 is fused to purify.

B. Evolution method—absorbs H_2S in CuSO_4 and ignites to CuO . S may be retained in both solid residue and liquid. Not applicable to white irons.

1893—SCHINDLER, WILH. *Ztschr. angew. Chem.*, Vol. 6, p. 11. "Beitrag zur Schwefelbestimmung im Eisen nach der Schwefelwasserstoffmethode."

Also in: *Chemisches Repertorium*, Vol. 18, p. 5.

J. Chem. Soc. Lond., Vol. 64, p. 389 (1893).

J. Soc. Chem. Ind., Vol. 12, p. 625 (1893).

J. I. S. I., (1893), p. 408.

Ztschr. anorg. Chem., Vol. 3, p. 395 (1893).

Central Blatt, (1893), p. 319.

Berichte, (1893), p. 161.

Results not accurate unless conc. HCl is used for evolution method.

Sample (10 grs.)	1.19 HCl Br in HCl (CO_2)	1.19 HCl H_2O_2	1.10 HCl Br in HCl	1.10 HCl H_2O_2
Pig iron	0.070% S	0.071% S	0.048% S	0.048% S
	0.071	0.067	0.045	0.048
	0.221	—	0.149	—
	0.216	—	0.157	—

1893—SCHNEIDER, L. *Oster. Zeit. Berg. Hütt.*, Vol. 41, p. 365. "Beiträge zur Chemischen Untersuchung des Stahles. Die Schwefelbestimmung."

Also in: *J. Chem. Soc. Lond.*, Vol. 66, Part 2, p. 162 (1894).

Ztschr. angew. Chem., (1893), p. 702.

J. I. S. I., (1893), p. 532.

Central Blatt, (1893), p. 623.

Discussion of evolution and oxidation methods. With enough acid and half-hour's boiling all S can be removed from residue; H_2S also not found in liquid. Oxidation methods inaccurate due to impurities in BaSO_4 ; purification of BaSO_4 makes a new and greater error. In evol. method it is not necessary to expel air; KMnO_4 is best absorbent.

1894—BAMBER, H. K. *J. I. S. I.*, Vol. 45, p. 319. "On the Analysis of Steel."

Also in: *J. Soc. Chem. Ind.*, Vol. 13, p. 665 (1894).

The Analyst, Vol. 22, p. 279 (1897).

200 grains of steel drillings are treated with a mixture of 4 ozs. of distilled water and 2.5 ozs. 1.42 HNO_3 ; after the violent action boil till all dissolved, add 1 oz. 10 per cent. Na_2CO_3 , boil, evaporate, ignite in platinum at dull red heat over Bunsen burner. The red powder is treated with $\frac{1}{2}$ oz. 10 per cent. Na_2CO_3 and evaporated to dryness, taken up with hot water containing $\frac{1}{2}$ per cent. Na_2CO_3 , filtered, washed with same, and BaSO_4 precipitated and weighed.

		S in rails
Steel 1	0.049 and 0.051% S
2	0.051 and 0.054
3	0.051 and 0.049
4	0.046 and 0.046
5	0.057 and 0.057

		S in spring steel
Steel 1	0.025 and 0.025 and 0.024% S

1894—GLADDING, THOMAS S. *J. Am. Chem. Soc.*, Vol. 14, p. 398. "On the Estimation of Sulphur in Pyrites."

Many analytical figures to determine sources of error. Nitrates give high results, chlorides no effect, iron makes results low, ferric hydroxide always drags down sulfur, barium sulfate is insoluble in ferric chloride solution.

- 1894—REIS, M. A. VON. *Stahl u. Eisen*, Vol. 14, p. 963. "Zur Bestimmung von Schwefel im Eisen."

Also in: *J. Chem. Soc. Lond.*, Vol. 68, Part 2, p. 527 (1895).

Ztschr. anorg. Chem., Vol. 8, p. 240 (1895).

Ztschr. angew. Chem., (1895), p. 29.

J. I. S. I., (1895), p. 509.

Central Blatt, (1895), p. 129.

Four pages of discussion with directions for evol. method as best. Uses const. boil. acid—1.09 sp. gr.—boils till liquor gets thick so as to get all S; absorbs H_2S in amm. H_2O_2 . To hasten pptn. of $BaSO_4$ evaps. to dryness or boils with $KMnO_4$. Says not to use CO_2 to sweep out H_2S because CO_2 expels $(NH_4)_2S$ from alk. solution.

- 1894—SLEEPER, J. F. *Chemical News*, Vol. 69, p. 63. "On the Precipitation of Barium Sulphate in the Presence of Silica, and the Decomposing Action of Hydrofluoric Acid on the Former."

$BaSO_4$ does not drag down SiO_2 when precipitated drop by drop, hot. HF decomposes $BaSO_4$ unless free H_2SO_4 is present; to free a $BaSO_4$ ppt. of SiO_2 have a little free H_2SO_4 on ppt.

- 1894—SPÜLLER, J., AND KAHLMANN, S. *Chem. Ztg.*, Vol. 18, p. 2039. "Bestimmung des Schwefels in Stahl und Eisen."

Also in: *J. Chem. Soc. Lond.*, Vol. 68, Part 2, p. 244 (1895).

Chemical News, Vol. 70, p. 239 (1895).

J. I. S. I., (1895), p. 512.

Central Blatt, (1895), p. 232.

Evol. method using HCl , 1.17, and 3 per cent. Na_2O_2 to absorb H_2S washed through with air passed first through $HgCl_2$ and alk. pyrogallol. Oxidizes with $KMnO_4$ and ppts. with $BaCl_2$. Gives cut of app. with condenser about neck of flask. Cooks sample from 45 mins. to 2.5 hrs.

Sample	Bromine	Sodium peroxide
White pig	0.068% S	0.067% S
Flusseisen	0.022	0.022
Schweisseisen	0.014	0.015
Martin steel	0.019	0.019
Acid Bessemer	0.039	0.036
Crucible steel	0.015	0.015

1895—ARNOLD, J. O. "*Steel Works Analysis.*" Whittaker & Co., London, 1895.

Pages 96 to 110 on S detn.

Several methods with cuts given; nothing new.

1895—CARNOT, A. "*Methodes D'Analyse des Fontes, des Fers et des Aciers.*" Dunod & Vicq, Paris, 1895.

Pages 82 to 96 on S detn. several methods given.

1895—CAMPREDON, LOUIS. *Compt. rend.*, Vol. 120, p. 1051.
"Dosage du soufre dans les fontes, les aciers et les fers."

Also in: *Chemical News*, Vol. 72, p. 15 (1895).

J. Chem. Soc. Lond., Vol. 68, p. 411 (1895).

J. Soc. Chem. Ind., Vol. 14, p. 889 (1895).

Ztschr. anal. Chem., Vol. 36, p. 391.

Ztschr. anorg. Chem., Vol. 10, p. 448.

J. I. S. I., Vol. 48, p. 595 (1895).

Central Blatt, (1895), p. 61.

Refers to and follows Rollet's method in general; gives calculations but no results.

Dissolves 2 to 10 grs. sample in dil. H_2SO_4 or dil. HCl , uses CO_2 and H_2 , absorbs in acid $\text{Zn}(\text{OAc})_2$; excess I_2 is run in and back titer with thio. after 2-3 mins. $\text{ZnS} + \text{I} = \text{ZnI} + \text{S}$. The H_2S and gases are passed through a heated tube.

1895—CARNOT, A. *Annales des Mines*, Vol. 8, p. 357. "Methodes d'analyse des fontes, des fers et des aciers."

Pages 438 to 452 devoted to S methods, practically all methods referred to and work of many men discussed. No new material.

- 1895—FORESTIER, A. *Bull. Soc. Chim. Paris*, Vol. 13, p. 586.
"Essai des aciers, fer et fontes par l'analyse chimique. Résumé de rapport présenté par M. Adolph Carnot."

Summarizes under three headings:

- A. Aqua regia,
HCl and Br,
KClO₃.
- B. Oxidation with perchlorates.
- C. Evolution as H₂S.

- 1895—JONSTORFF, JÜPTNER VON. "*Fortschritte im Eisenhütten-Laboratoriums*." A. Felix, Leipzig, 1895.

Pages 115 to 142 review S detn.

- 1895—KONINCK, L. L. DE. *Chem. Ztg.*, Vol. 19, p. 502. "Vorschlag zur Bestimmung von Schwefel in Eisensorten."

Also in: *J. Soc. Chem. Ind.*, Vol. 14, p. 597 (1895).

J. Chem. Soc. Lond., Vol. 68, p. 528 (1895).

J. I. S. I., Vol. 48, p. 597 (1895).

Adds SnCl₂ or Sn to flask to prevent oxidation of FeO;
conc. HCl must be used to prevent formation of SnS.

- 1895—LUNGE, G. *J. Am. Chem. Soc.*, Vol. 17, p. 181. "On the Estimation of Sulphur in Pyrites."

Also in: *Chemical News*, Vol. 71, p. 132.

Reply to Gladding's method. No S need be left in a Fe(OH)₃ ppt. if it is properly washed. Fresenius proved that FeCl₃ dissolves BaSO₄. Some results to confirm.

- 1895—PHILLIPS, FRANCIS C. *J. Am. Chem. Soc.*, Vol. 17, p. 891.
"The Evolution Method for the Determination of Sulphur in White Cast Iron."

Also in: *J. Soc. Chem. Ind.*, Vol. 15, p. 218 (1896).

Chemical News, Vol. 75, p. 194.

Ztschr. angew. Chem., (1897), p. 65.

Ztschr. anorg. Chem., Vol. 15, p. 373 (1897).

J. I. S. I., Vol. 50, p. 443 (1896).

Methyl sulfid and other organic cpds. given off with H_2S in evol. method. To decompose the organic S cpds. pass gases through hot tube and then absorb H_2S in HCl and Br . Carries out evol. slowly 2-2.5 hrs.

Sample	Evolution	Evolution with hot tube	Aqua Regia (Blair)
Iron A	0.059	0.096	0.101
	0.046	0.095	0.098
	0.050	0.104	0.096
	0.050	0.104	0.099
	0.054	0.099	0.100
	0.055	0.100	0.102
	—	0.092	0.102
	—	0.105	0.104
	—	0.098	—
	—	0.101	—
Mean	0.052	0.099	0.100
Iron B	0.100	0.183	0.173
	0.101	0.178	0.170
	0.087	0.175	0.168
	0.099	0.181	0.170
	0.092	0.177	0.174
	0.084	0.188	0.171
Mean	0.094	0.180	0.171

1895—READ, E. J. *Chemical News*, Vol. 72, p. 299. "Apparatus for the Estimation of Sulphur in Iron."

Also in: *Ztschr. anorg. Chem.*, Vol. 15, p. 373.

Central Blatt, (1896), p. 391.

Evolution flask provided with sep. funnel and connection (rubber) to a small flask containing abs. liquid and column of beads in tube above flask.

1895—RICHARDS, T. W., AND PARKER, H. G. *Ztschr. anorg. Chem.*, Vol. 8, p. 413. "Über die Einschliessung von Baryumchlorid durch Baryumsulfat."

Also in: *Chemical News*, Vol. 72, p. 281 (1895).

A 10-page article with these conclusions:

1. $BaCl_2$ included with $BaSO_4$ makes app. error.

2. Error increases with conc. and with HCl and by adding SO_4 .
3. Error balances solubility of BaSO_4 .
4. Detn. Cl and deduct equiv. BaCl_2 to correct.

1896—AUCHY, GEORGE. *J. Am. Chem. Soc.*, Vol. 18, p. 406.

"Drown's Method of Determining Sulphur in Pig Iron."

Also in: *J. Soc. Chem. Ind.*, Vol. 15, p. 381 (1896).

J. I. S. I., Vol. 50, Part 2, p. 445 (1896).

Bull. Soc. Chim., Vol. 16, p. 1417 (1896).

Ztschr. anorg. Chem., Vol. 15, p. 373 (1897).

Central Blatt, (1896), p. 1080.

Berichte, Vol. 29, p. 1013 (1896).

Slight modification of Drown's method; evol. of H_2S and absorption in KOH and KMnO_4 , evaps. to dryness, takes up in HCl and ppts. BaSO_4 . Uses dil. HCl for evolution. 35 results demonstrates precision of method using H_2SO_4 as source of BaSO_4 ; 12 results show that free HCl apparently dissolves BaSO_4 slightly; 6 show that standing 1 hour is not long enough to get all BaSO_4 ; 13 results show that oxalic acid does not affect BaSO_4 .

Using H_2SO_4 :

			BaSO ₄ stands 1 hour		
	S taken	S found		S taken	S found
1	0.237	0.238	1	0.029	0.024
2	0.121	0.119	2	0.014	0.007
3	0.057	0.057	3	0.029	0.023
4	0.029	0.033	4	0.121	0.115
	Over 5% free HCl		5	0.060	0.056
1	0.014	0.014	6	0.045	0.041
2	0.029	0.029		Excess oxalic acid	
3	0.121	0.115	1	0.014	0.014
	5 cc. free HCl		2	0.029	0.029
1	0.121	0.112	3	0.121	0.118
2	0.121	0.114	4	0.029	0.029
3	0.237	0.234	5	0.060	0.059
4	0.057	0.054	6	0.045	0.046
5	0.029	0.024	7	0.090	0.090
6	0.014	0.010	8	0.060	0.060
7	0.029	0.028	9	0.090	0.090
8	0.029	0.026	10	0.029	0.029
9	0.014	0.010	11	0.014	0.014
			12	0.121	0.119
			13	0.237	0.239

1896—BOUCHER, G. G. *Chemical News*, Vol. 74, p. 76. "Estimation of Sulphur in Cast Iron or Steel."

Also in: *J. I. S. I.*, Vol. 50, Part 2, p. 444 (1896).

Ztschr. anorg. Chem., Vol. 15, p. 373 (1896).

Central Blatt, (1896), p. 684.

Dissolves sample in strong Cu-Amm-Chloride soln., filters off residue to treat with aq. reg. or Br water; S detd. as BaSO_4 .

	Sample	Nitric-hydrochloric	Cu-amm-chloride	
1	Bessemer iron	0.035	0.041	
2	Bessemer iron	0.012	0.021	
3	Bessemer iron	0.022	0.024	
4	Bessemer iron	0.023	0.023	
5	Bessemer iron	—	0.020	0.021
6	Mottled iron	0.185	0.192	0.192

1896—FOULK, C. W. *J. Am. Chem. Soc.*, Vol. 18, pp. 793-807.

"The Effect of an Excess of Reagent in the Precipitation of Barium Sulphate."

17 series of experiments run. Most pertinent conclusions:

Pptg. with BaCl_2 gives fine ppt. in presence of HCl.

Use large excess of BaCl_2 for complete pptn.

Increase BaCl_2 with HCl.

More HCl used the coarser and more cryst. the ppt.

In conc. solns. ppt. impure with BaCl_2 not removed by washing.

Concordant results are not necessarily accurate.

1896—FRESENIUS, R., AND HINTZ, E. *Ztschr. anal. Chem.*, Vol. 35, p. 170. "Ueber eigenthümliche Löslichkeitsverhältnisse des schwefelsauren Baryts."

Also in: *Chemical News*, Vol. 73, p. 276.

A 13-page article giving much fundamental data.

"In precipitating sulfuric acid by an excess of barium chloride from such hydrochloric acid (10 per cent.) we must remember that in 100 cc. of filtrate 1 mg. of barium

sulfate remains in solution."

Solubility of BaSO_4 .

Water

1 part BaSO_4 in 100,000

1 part BaSO_4 in 400,000 BaCl_2 or H_2SO_4 in excess

8% NH_4Cl

1 part BaSO_4 in 10,000

1 part BaSO_4 in 400,000 H_2SO_4 excess

1 part BaSO_4 in 50,000 BaCl_2 excess

2.3% NH_4Cl

1 part BaSO_4 in 22,000

1 part BaSO_4 in 80,000 BaCl_2 excess

1 part BaSO_4 in 400,000 H_2SO_4 excess

2.3% NaCl

1 part BaSO_4 in 22,000

1 part BaSO_4 in 80,000 NaCl excess

1 part BaSO_4 in 400,000 H_2SO_4 excess

8% HNO_3

1 part BaSO_4 in 7,300

1 part BaSO_4 in 33,000 HNO_3 excess

1 part BaSO_4 in 400,000 H_2SO_4 excess

8% HCl

1 part BaSO_4 in 7,300

1 part BaSO_4 in 33,000 HCl excess

1 part BaSO_4 in 400,000 H_2SO_4 excess

1896—GLADDING, THOMAS S. *J. Am. Chem. Soc.*, Vol. 18, p. 446.
"On the Estimation of Sulphur in Pyrites."

Also in: *J. Chem. Soc. Lond.*, Vol. 70, p. 622 and 672.

Contents that sudden pptn. of BaSO_4 causes high results as against Lunge who asserts that it makes no difference how the BaCl_2 is added. Admits BaCl_2 soluble in HCl but errors not balanced.

1896—LUCAS, MAURICE. *Bull. Soc. Chim. Paris*, Vol. 17, pp. 144-152. "Les Methodes de Dosage du Phosphore et du Soufre dans le Fer, l'Acier et la Fonte."

Also in: *J. Chem. Soc. Lond.*, Vol. 74, Part 2, p. 483 (1898).

J. I. S. I., Vol. 54, p. 559 (1898).

Central Blatt, (1897), p. 435.

Evolves H_2S with H_2SO_4 and HCl and passes through hot tube into alk. lead soln. The pptd. PbS is filtered off, washed, dissolved in HNO_3 , neutralized with NaOH and the Pb estimated colorimetrically by author's process. Gives cut of apparatus. Uses 1 gram sample and says always gets constant and delicate results.

1896—MATTHEWMAN, F. A. *J. West Scot. I. S. I.*, Vol. 3, pp. 1-76. Original not available. *J. I. S. I.*, Vol. 49, Part 1, p. 537 reads: "F. A. Matthewman has instituted an exhaustive inquiry into the present methods of estimating sulphur in iron and steel."

1896—MORGAN, J. J. *Chemical News*, Vol. 74, p. 257. "Estimation of Sulphur in Cast Iron or Steel."

Discusses Boucher's method saying it is repetition of Meincke's.

1896—PHILLIPS, FRANCIS C. *J. Am. Chem. Soc.*, Vol. 18, p. 1079. "The Determination of Sulphur in Cast Iron."

Also in: *J. Chem. Soc. Lond.*, Vol. 72, Part 2, p. 431 (1897).

Ztschr. anorg. Chem., Vol. 18, p. 394 (1898).

Bull. Soc. Chim. Paris, Vol. 18, p. 622.

Chemical News, Vol. 75, p. 194 (1897).

Central Blatt, (1897), p. 303.

Oxidizes sample with fusion mixture of 45 parts NaNO_3 , 45 parts Na_2O_2 and 10 parts Na_2CO_3 ; residue is digested with Br water. BaSO_4 is pptd. in the evaporated and acidified filtrate.

"An indispensable condition of success in the use of the method is found in the extreme fineness of the iron. In the case of white irons the fineness of the powder has been secured by crushing in a steel mortar until the powder passed through a sieve of bolting sheeting or bolting cloth.

Some grey irons cannot be crushed or ground. For grey irons, however, the evolution method answers all requirements." P. fuses 1.5 grs. sample in platinum with 8 grs. of mixture for 20 mins.

White iron, sifted		White iron, sifted	
Fusion method	HNO ₃ method	Fusion method	HNO ₃ Method
0.112% S	0.101% S	0.155% S	0.143% S
0.112	0.098	0.150	0.149
0.111	0.096	0.130	0.143
0.107	0.099	0.139	0.147
0.114	0.100	0.166	
0.114	0.102	0.156	0.145
0.106	0.102	0.156	
0.108	0.104	0.161	
0.107		0.151	
0.103	0.100		
0.109		0.151	
Ferromanganese, sifted		Gray iron, unsifted	
0.022% S	0.012% S	0.034% S	0.027% S
0.027	0.013	0.030	0.030
0.018	0.012	0.036	0.026
0.018	0.010	0.034	0.028
0.018		0.033	0.028
0.019	0.012	0.034	0.022
0.016			
0.020		0.033	0.027

1896—SCHULTE, WILHELM. *Stahl u. Eisen*, Vol. 16, p. 865.
 "Eine Neue Methode zur Bestimmung des Schwefels in Eisen."

Also in: *J. Chem. Soc. Lond.*, Vol. 74, Part 2, p. 45 (1898).

Chemical News, Vol. 75, p. 47 (1897).

Ztschr. anorg. Chem., Vol. 15, p. 373.

Central Blatt, (1896), p. 1132.

Evol. method passing gases through condensing tube into Cd(OAc)₂ sol., CuSO₄ is added, the CuS filtered off and ignited to CuO. Connections of rubber.

	Gr.	Gr.	Gr.	Gr.	Gr.	Gr.	Gr.
Pure ZnS	0.1500	0.1000	0.0500	0.0200	0.0100	0.0050	0.0010
Calc. CuO	0.1225	0.0817	0.04085	0.01635	0.00817	0.00408	0.00081
Found CuO	0.1220	0.0817	0.0408	0.0164	0.0082	0.0041	0.0008

	Br-BaSO ₄ method	CdS-CuO method
Iron sulfid	23.83 %	23.85 %
Gray pig	0.422	0.424
Wrought iron	0.203	0.202
Puddle iron	0.190	0.193
Thomas pig	0.051	0.052
Bessemer pig	0.026	0.026
Tool steel	0.016	0.016
Steel	0.108	0.117
Thomas iron	0.061	0.060
Rohstahl iron	0.052	0.052
Spiegeleisen	0.050	0.050
Bessemer iron	0.028	0.026
Bessemer gray iron.....	0.014	0.016
Ferromanganese	0.005	0.005

1897—BLAIR, A. A. *J. Am. Chem. Soc.*, Vol. 19, p. 114. "The Determination of Sulphur in Pig Iron."

Also in: *J. Chem. Soc. Lond.*, (1897), Part 2, p. 594.
Central Blatt, (1897), p. 942.

Review of methods, mentioning work of Bamber and Phillips. Four forms of sulfur in iron given:

- A. S evolved as H₂S.
- B. S evolved as other compounds.
- C. S not acted upon by HCl but by HNO₃ or aq. reg.
- D. S unaffected by HCl, HNO₃ or aq. reg.

S in one sample:

S by oxidation.....	0.032%
S evolved	0.000
S by hot tube.....	0.005
S in residue.....	0.057
Total	0.062%

Oxidation by Shimer.....	0.042%
Bamber's method	0.064
S in residue by oxidation.....	0.030

1897—BOUCHER, G. G. *Chemical News*, Vol. 75, p. 121. "Volumetric Estimation of Sulphur in Iron, Steel and Sulphides of Iron."

Also in: *Ztschr. anorg. Chem.*, Vol. 18, p. 394.
Central Blatt, (1897), p. 769.

The iodide is the only volumetric method in general use; as the iodine sol. has the great disadvantage of not keeping it is proposed to evolve the H_2S into a solution of $FeCl_3$ and titrate with $K_2Cr_2O_7$.

3.065 grs. $K_2Cr_2O_7$ in 1,000 cc. = 0.001 gr. S per 1 cc.

	Gravimetric	Dichromate titer
Bessemer iron—I	0.041	0.038
2	0.015	0.017
3	0.020	0.023
4	0.028	0.030
Mottled iron—I	0.312	0.320
2	0.411	0.399
3	0.295	0.296
4	0.384	0.387

1897—CAMPREDON, LOUIS. *Stahl u. Eisen*, Vol. 17, p. 486. "Bestimmung des Schwefels in Eisen."

Also in: *J. Chem. Soc. Lond.*, Vol. 74, Part 2, p. 350 (1897).

Monit. Sci., Vol. 12 (4), p. 778 (1898).

J. Soc. Chem. Ind., Vol. 17, p. 1184 (1898).

J. I. S. I., (1897), p. 503.

Ztschr. angew. Chem., (1897), p. 566.

Ztschr. anorg. Chem., Vol. 18, p. 393 (1898).

Central Blatt, (1897), p. 383.

Criticises Schulte's method; recommends hot tube; prefers to absorb in zinc acetate. Uses condenser over flask but rubber connections.

Sample	Evolved	By heating gases	Diff.
1	0.002%	0.013%	0.011%
2	0.039	0.056	0.017
3	0.102	0.126	0.024
4	0.029	0.053	0.024
5	0.058	0.076	0.018
6	0.032	0.060	0.028
7	0.041	0.059	0.018
8	0.045	0.057	0.012
9	0.022	0.043	0.021
10	0.029	0.056	0.027
11	0.042	0.058	0.016
12	0.002	0.033	0.031
13	0.006	0.018	0.012
14	0.012	0.031	0.019
15	0.039	0.065	0.026
16	0.376	0.379	0.003
17	0.011	0.127	0.016
18	0.190	0.204	0.014
19	0.008	0.038	0.030
20	0.007	0.015	0.008
21	0.056	0.084	0.028
22	0.241	0.254	0.013

1897—CARNOT, A., AND GOUTAL. *Compt. rend.*, Vol. 125, p. 75.
 “Sur l’emploi des sels cuivriques pour préparer le dosage
 de divers éléments dans les fontes et les aciers.”

Also in: *J. Chem. Soc. Lond.*, Vol. 72, Part 2, p. 520
 (1897).

Ann. de Chim. Anal., 11 (16), p. 301.

The Analyst, Vol. 22, p. 300 (1897).

Dissolve steel in sol. of $\text{KCl} \cdot \text{CuCl}_2$ acidified to hasten
 action; treat residue with HCl ; S is oxidized with Br and
 pptd. as BaSO_4 .

1897—CARNOT, A., AND GOUTAL. *Compt. rend.*, Vol. 125, p. 213.
 “Recherches sur l’état au se trouve dans les fontes et aciers
 les éléments autres que le carbone.”

Also in: *Ann. de Chim. Anal.*, (1897), p. 301.

Bull. Soc. Chim. Paris, Vol. 17, p. 1054.

States that Berzelius originated solution of iron in CuCl_2 . After attack with CuK_2Cl_4 all S is in insoluble residue. Filter, treat residue with $\text{HCl} + \text{Br}$, warm, boil, filter, neutralize with NH_4OH , acidify with HCl and ppt. with BaCl_2 .

1897—DUDLEY, C. B. *J. Am. Chem. Soc.*, Vol. 19, p. 93. "Some Present Possibilities in the Analysis of Iron and Steel."

Also in: *Chemical News*, Vol. 75, p. 283 (1897).

Bull. Soc. Chim. Paris, Vol. 18, p. 675.

Review Methods. "It seems not too much to say that it is hazardous to use the evolution method on pig or cast iron, even when fusion of the residue is employed." Says that for evolution method on steels one operator can make 2 determinations in 2 hours with 2 sets of app.; with 4 sets 1 operator can make 12 detns. a day. Oxidation method requires 5 hours for 2 detns. and 1 operator can make only 10 or 12 detns. a day. If BaSO_4 is fused to purify $\frac{1}{3}$ less work can be done.

1897—HERTING, OTTO. *Chem. Ztg.*, Vol. 21, p. 87. "Beitrag zur Bestimmung des Schwefels in Eisensorten."

Also in: *Chemical News*, Vol. 75, p. 109 (1897).

Ztschr. anorg. Chem., Vol. 18, p. 394 (1898).

Central Blatt, (1897), p. 514.

Follows Morrell's scheme, but titrates H_2S liberated from CdS with I_2 . Thinks that air does not separate S, so H_2 or CO_2 not necessary. Says Wiborgh's method requires too small a sample.

Sample	Br method	Iodine titer	Wilborgh's
1	0.0410% S	0.0416% S	0.035% S
2	0.0333	0.0340	0.035
3	0.0152	0.0156	0.012
4	0.0181	0.0178	0.012

S present in residues from 1 and 2, but no weighable BaSO_4 found.

1897—JOHNSON, E. S. *J. Am. Chem. Soc.*, Vol. 19, p. 288.

"Some Apparatus for the Technical Analytical Laboratory."

Also in: *Ztschr. angew. Chem.*, (1897), p. 937.

A suitable wooden frame supports evolution flasks over burners; 3-hole rubber stoppers accommodate connection to hydrogen, separatory funnels and bulbed exit tube to absorption tubes. Absorption tubes are 1" x 10" and lipped.

1897—LAUDIS, E. K. *J. Am. Chem. Soc.*, Vol. 19, p. 261.
"Standard Iodine Solution for Sulphur Determinations."

Also in: *Chemical News*, Vol. 75, p. 218 (1897).

Similar to Payne of 1892. States standard reactions and calculations.

1897—MEADE, R. K. *J. Am. Chem. Soc.*, Vol. 19, p. 581. "A New Apparatus for Sulphur Determinations in Iron and Steel and a Useful Form of Wash-Bottle."

Also in: *J. Soc. Chem. Ind.*, Vol. 16, p. 934 (1897).

Central Blatt, (1897), p. 634.

Wooden stand fitted up to support evolution flask and 2 absorption columns in series; latter have stop cocks at bottom to drain liquid to beakers for titration.

1897—SCHULTE, WILHELM. *Stahl u. Eisen*, Vol. 17, p. 489.
"Bestimmung des Schwefels in Eisen."

Also in: *J. Chem. Soc. Lond.*, Vol. 74, Part 2, p. 350 (1898).

Chemical News, Vol. 75, p. 47.

Ztschr. anorg. Chem., Vol. 18, p. 394.

Ztschr. angew. Chem., (1897), p. 566.

Central Blatt, (1897), p. 383.

Discusses evolution method, especially ways to oxidize H_2S . Supplies cut of apparatus with furnace to heat gases; uses 1-2 HCl and absorbs in $Cd(OAc)_2$ to which $CuSO_4$ is added to ppt. CuS which is ignited to CuO and weighed. Asserts one can no longer omit to heat gases when using evol. method. Rubber connections.

Sample	Method	Without heating	Heating gases	Total	% increase
Mill iron	Br-oxid.	0.1577	0.0094	0.1671	5.9
	H ₂ O ₂ -oxid.	0.1654	0.0145	0.1800	8.8
	CdS-CuO	0.1673	0.0137	0.1810	8.2
Steel	Br-oxid.	0.1190	0.0241	0.1431	20.2
	H ₂ O ₂ -oxid.	0.1176	0.0258	0.1435	22.0
	CdS-CuO	0.1253	0.0147	0.1400	11.5
Foundry iron	Br-oxid.	0.0660	0.0030	0.0690	4.6
	H ₂ O ₂ -oxid.	0.0877	0.0040	0.0917	4.6
	CdS-CuO	0.0969	0.0040	0.1010	4.1
Wrought iron	Br-oxid.	0.0700	0.0135	0.0835	19.3
	H ₂ O ₂ -oxid.	0.0693	0.0113	0.0806	16.5
	CdS-CuO	0.0654	0.0089	0.0743	13.5

Ascribes irregularities in total S to segregation in samples.

White iron	0.1923	0.0022	0.1945	1.1
	0.0897	0.0072	0.0969	8.1
	0.0671	0.0081	0.0752	12.0
Spiegel	0.0671	0.0048	0.0719	7.2
	0.0533	0.0065	0.0598	12.1
	0.0206	0.0117	0.0323	52.0
Foundry iron	0.1341	0.0073	0.1414	5.4
Thomas iron	0.0630	0.0101	0.0731	16.0
Bessemer iron	0.0356	0.0117	0.0473	33.0
Gray iron	0.0186	0.0095	0.0281	51.0
Basic, foundry iron.....	0.1010	0.0008	0.1018	0.8
	0.0768	0.0008	0.0776	1.0
	0.0695	0.0012	0.0707	1.7
	0.0553	0.0020	0.0573	3.6
	0.0218	0.0028	0.0246	13.0
Silicon iron	0.0218	0.0016	0.0234	7.4
Swedish iron	0.0161	0.0019	0.0180	12.0
Ferromanganese	0.0056	0.0016	0.0072	28.0
File steel	0.0309	0.0117	0.0426	38.0
English tool steel.....	0.0113	0.0085	0.0198	75.0
	0.0123	0.0095	0.0218	77.0
	0.0085	0.0068	0.0153	80.0
German fine steel.....	0.0044	0.0024	0.0068	54.0
Tungsten steel	0.0048	0.0012	0.0060	25.0

1898—ENG. SOC. WEST. PA. Book—“*Methods for the Analysis of Ores, Pig Iron and Steel.*” Chemical Pub. Co., Easton, Pa., 1898.

Brief outlines of methods used in several laboratories; uncritical.

1898—T., J. *Chemical News*, Vol. 78, p. 294. "Blank Tests."

Deprecates limited and inaccurate use of blanks in detn. of S in iron and steel.

Gets blank obtained by deducting the BaSO_4 of a large sample from twice the BaSO_4 of half samples, all carried out with identical amts. of reagents.

BaSO_4 (A) = BaSO_4 in A grams = Fe + blank (1)

BaSO_4 (2A) = BaSO_4 in 2A grams = Fe + blank (2)

(1) \times 2 = 2 BaSO_4 (A) = BaSO_4 in 2A grams + 2 blanks (3)

(3) — (2) = BaSO_4 due to blank.

This blank is usually lower than blank from same volume of acids and Na_2CO_3 .

1898—FRANKE, E. *Stahl u. Eisen*, Vol. 18, p. 326. "Zur Bestimmung des Schwefel in Eisen."

Also in: *Ztschr. angew. Chem.*, Vol. 11, p. 395 (1898).

Central Blatt, (1898), p. 1307.

Relates experience with different methods; decides Schulte's most accurate. Uses special apparatus and gets following results. Flask arm has condenser with no rubber connections at the flask.

No.	Art der Probe	Brom- Methode % S	H_2O_2 - Methode % S	Cadmium Cu O-Methode % S	Durch nachtrugl. Gluhen der Gase % S	Gesamt-saus- der Cadmium- CuO-Methode nactr. Gluhen % S	% sog. organ. S. des Gesamt-S
1	Weiceer Thomasstahl	0.036	0.040	0.063	—	0.036	—
2		0.108	0.127	0.110	—	0.110	—
3		0.058	0.061	0.057	—	0.057	—
4		0.063	0.066	0.066	—	0.056	—
5		0.064	0.067	0.065	—	0.065	—
6		0.094	0.106	0.098	—	0.088	—
7	Wolframstahl	nicht bestimmt	nicht bestimmt	0.0121	gering-	0.0121	—
8	Martinstahl			6.0477	Spuren	0.0477	—
9	Chromsthl			0.0057	0.0016	0.0073	28.07
10	Werkzeugstahl			0.0065	0.0022	0.0087	33.84
11	Bessemerstahl			0.071	ser. Sp.	0.071	—
12	Ferrosilicium			0.0243	—	0.0243	—
13	Holzkohleneisen			0.0057	Spur.	0.0057	—
14	Thomasrobleisen			0.0695	0.0022	0.0715	2.88
15	"	0.0741	0.067	0.0695	—	0.0715	—
16	"	0.0208	0.013	0.0259	—	0.0257	—
17	"	0.1744	0.167	0.1689	Spur	0.1685	—
18	"	0.6890	0.068	0.0711	—	0.0719	—
19	"	0.0664	0.064	0.0719	Spur	0.0719	—
20	"	0.088	0.088	0.1051	—	0.1051	—
21	"	0.1046	0.107	0.1034	—	0.1034	—
22	" grau	0.0345	0.041	0.0461	—	9.0461	—
23	" gemischt	0.0579	0.056	0.0582	Spur	0.0582	—
24	" weit's	0.0689	0.078	0.0776	—	0.0776	—
25	"	0.1123	0.102	0.1034	—	0.1034	—
26	Paddelroheisen	nicht best	nicht best	0.0614	—	0.0614	—
27	Giefsereiroheis.	0.0794	0.084	0.4923	—	0.4923	—
28	"	0.0776	0.0776	0.0776	—	0.0776	—

1899—AULICH. *Stahl u. Eisen*, Vol. 19, pp. 878-879. "Schwefel in Eisenerzen und Eisenhüttenerzeugnissen."

Also in: *J. I. S. I.*, (1899), p. 486.

Reviews methods to get pure BaSO_4 . Fe_2O_3 always found in BaSO_4 ppt. Avoided by boiling freshly pptd. BaSO_4 with conc. HCl after decanting off liquor, then add more BaCl_2 . Even then not entirely purified.

Other proposals:

1. Ppt. Fe with NH_3 and then ppt. BaSO_4 (iron may be filtered off or not) dissolve $\text{Fe}(\text{OH})_3$ with HCl . (Lunge.)
2. Use organic acid, as oxalic. (Küster and Thiel.)
3. Reduce to ferrous iron. (Meineke.) Sn in BaSO_4 after using SnCl_2 . Meineke prefers Zn.
4. Fusion processes; best as comparison methods; $\text{Na}_2\text{CO}_3 + \text{KClO}_3$.
5. Dissolve in CuCl_2 and oxidize residue.

1899—CROBAUGH, F. L. *Iron Trade Review*, Vol. 32, pp. 12-13. "Methods for the Iron Laboratory—IV. Sulphur."

Also in: *J. I. S. I.*, (1899), p. 486.

5 grams sample dissolved in 70 cc. HCl , sp. gr. 1.10, cold, when evolution slows down heat gradually for 20 min.; absorb in CdCl_2 and titrate with iodine.

1899—HERTING, O. *Chem. Ztg.*, Vol. 23, p. 768. "Beitrag zur Bestimmung des Schwefels in Eisensorten."

Also in: *J. Chem. Soc. Lond.*, Vol. 76, p. 804.

J. I. S. I., Vol. 56, Part 2, p. 484 (1899).

Central Blatt, (1899), p. 885.

Review of methods and recommends processes. Says all evol. methods give low results unless pass gases through heated tube. Methods of Campredon and Schulte good; Blair's fusion process is satisfactory while Wiborgh's is good for routine work. Mentions that Heidenreich re-

duces Fe''' with SnCl_2 before precipitating (Heidenreich was working on S in pyrites).

- 1899—KUSTER, F. W., and THIEL, A. *Ztschr. anorg. Chem.*, Vol. 19, p. 97. "Ueber die Bestimmung der Schwefelsäure bei gegenwart von Eisen."

Also in: *J. Chem. Soc. Lond.*, (1901), p. 124.

Ztschr. anorg. Chem., Vol. 25, p. 319 (1900).

Uses oxalic and tartaric acids to prevent iron coming down with BaSO_4 .

	BaSO_4				Average
20 cc H_2SO_4 + HCl + BaCl_2	0.7135	0.7120	0.7130	0.7135	0.7130
+ FeCl_3	0.6540	0.6690	0.6720	0.6576	0.6632
+ FeCl_3 pptd. with NH_3	0.7133	0.7109	0.7115	0.7142	0.7125
+ FeCl_3 + Amm. Ox.	0.7115	0.7129	—	—	0.7122
+ FeCl_3 + Amm. Tart.	0.7144	0.7117	0.7116	0.7143	0.7130

- 1899—MEINECKE, C. *Ztschr. anal. Chem.*, Vol. 38, pp. 209-217.

"Ueber die Bestimmung der Schwefelsäure, mit besondere Berücksichtigung der Bestimmung des Schwefels in Eisen-erzen und Eisenhüttenproducten."

Also in: *J. I. S. I.*, (1899), p. 490.

J. Chem. Soc. Lond., Vol. 76, p. 518.

Nearly 8 pages of discussion concluding that reducing iron with Zn and his CuCl_2 method give identical results. Both of these with other methods give good results on pyrites residues.

Pig iron	CuCl_2 method	Zn reduction method
a	0.332% S	0.323% S
b	0.312	0.315
c	0.286	0.303
d	0.289	0.280

- 1899—MOORE, M. J. *J. Am. Chem. Soc.*, Vol. 21, p. 972. "Notes on the Determination of Sulphur in Pig Iron."

Also in: *J. Chem. Soc. Lond.*, Vol. 77, Part 2, p. 106 (1900).

The Analyst, Vol. 25, p. 82 (1900).

J. Soc. Chem. Ind., (1900), p. 72.

J. I. S. I., Vol. 57, p. 434 (1900).

Central Blatt, (1899), p. 1139.

Results obtained on "chilled shot samples" by both oxidation and evolution methods differ more than samples of ordinary metal. Gives results on 10 samples. Does not recommend volumetric method; it gives higher results on sand cast samples than on chilled ones.

1899—RIEMER, ADOLF.. *Stahl u. Eisen*, Vol. 19, p. 1064. "Bestimmung des Schwefels in Roh- und Flusseisen."

Also in: *J. Chem. Soc. Lond.*, Vol. 77, Part 2, p. 309 (1900).

J. I. S. I., (1900), p. 434.

Central Blatt, (1900), p. 61.

Thinks Wiborgh's method untrustworthy; prefers $\text{Cd}(\text{OAc})_2$ and excess iodine, then back titer with thiosulphate.

Sample	Br-HCl	Iodine-thio.	Wiborgh's
Pig iron	0.12	0.12	0.06 0.08
No. 2 iron.....	0.09	0.092	0.03 0.06
	H_2O_2		0.04 0.035
Ingot iron	0.080	0.072	0.04
	0.121	0.134	0.04
	0.213	0.198	0.12
Pig iron	0.067	0.069	0.04
	0.116	0.113	0.07
	0.133	0.128	0.06
	0.229	0.237	0.14

1899—THILL, J. *Ztschr. anal. Chem.*, Vol. 38, p. 342. "Die Massanalytische Bestimmung des Schwefels in Roheisen, Stahl. u. s. w. durch arsenige Säure."

Also in: *Chem. Ztg.*, Vol. 23, p. 1015 (1899).

Chemical News, Vol. 81, p. 54 (1900).

J. Chem. Soc. Lond., Vol. 76, p. 693 (1899).

J. Soc. Chem. Ind., Vol. 18, p. 947 (1899).

The Analyst, Vol. 24, p. 302 (1899).

Central Blatt, (1899), p. 493.

Receives H_2S in 25 cc. $\text{N}/10 \text{ As}_2\text{O}_3$ + 50 cc. cold sat. Na_2CO_3 . Don't evolve too rapidly; pass CO_2 through till all H_2S is over. Add few drops of HCl , dilute to 500 cc. and filter. Titrate 100 cc. of filtrate with $\text{N}/50$ iodine, solution being made alk. with Amm. Carb. and starch for

sharp endpoint. Uses apparatus of Franke or Wiggert and von Reis.

	H ₂ O ₂	As ₂ O ₃
Thomas pig	0.108% S	0.105% S
	0.081	0.083
	0.095	0.090
	0.148	0.148
Puddle pig	0.482	0.476
	0.312	0.310
	0.568	0.559

1900—LEDEBUR, A. Book—"Leitfaden für Eisenhütten-Laboratorien." F. Vieweg & Sohn, Braunschweig, 5th Ed., 1900. Several later editions. Gives several methods and cuts of Schulte's and Corleis' apparatus.

1900—BLOUNT, B. *The Analyst*, Vol. 25, pp. 141-146. "The Determination of Carbon and Sulphur in Steel."

Also in: *J. Chem. Soc. Lond.*, Vol. 77, Part 2, p. 574 (1900).

Central Blatt, (1900), p. 287.

Sulphur cannot be determined by direct combustion in oxygen. Cores of pieces contain excess S and as much as 20% remains even when heated to 1,200° C.

Sample of steel:

S volatilized	0.006%
From Fe ₃ O ₄	0.041
In Fe kernel	0.017
Total	0.064%

1901—ANTONY, U. *Gaz. chim. ital.*, Vol. 31, p. 274. "Determinazione dello solfo e del fosforo nei prodotti siderurgici."

Also in: *Ztschr. anorg. Chem.*, Vol. 32, p. 123 (1902).

J. Chem. Soc. Lond., (1902), p. 47.

J. Soc. Chem. Ind., Vol. 21, p. 71 (1902).

J. I. S. I., Vol. 61, p. 649 (1902).

Central Blatt, (1901), p. 1171.

5 grams of very finely divided sample heated to redness with 40 grams of mixture of 4 parts MnO_2 , 1 part KMnO_4 and 2 parts of Na_2CO_3 ; stirred with Pt wire. Water extract is acidified with HNO_3 , FeCl_3 added and P pptd. with NH_4OH and NH_3 ; BaSO_4 pptd. in filtrate.

1900—FRESENIUS, DR. C. R. Book—“*Quantitative Chemical Analysis*.” John Wiley & Sons, New York, 1900. Edited by Allen and Johnson.

Evolution method is given on pages 760 to 763; 10 grs. sample dissolved in dil. HCl and the H_2S is received in amm. AgNO_3 . Both the AgS and residue are treated with aq. reg. and the H_2SO_4 pptd. from clear solns. with BaCl_2 .

1901—AUCHY, GEORGE. *J. Am. Chem. Soc.*, Vol. 23, p. 147. “Determination of Sulphur in Wrought Iron and Steel.”

Also in: *J. Chem. Soc. Lond.*, (1901), p. 420.

J. Soc. Chem. Ind., (1901), p. 620.

“From the above table it seems that sometimes the evolution method is accurate and sometimes not; it is impossible, therefore, to find a correction that will be a true one in all cases and the practice common in western Pennsylvania of standardizing the iodine solution against a standard steel of the same kind as those to be worked on must also fail at times, although it is perhaps not unlikely that the error is more regular and constant with steels than with irons. The best that can be done seems to be to note the greatest error in a series of tests and use one-half this error as a correction. According to this plan the writer, when using this method, increases his results one-fourth; thus, for instance, 0.020 per cent. is called 0.025 per cent., and 0.012 per cent. is made 0.015 per cent. This, of course, is far from satisfactory, but seems to be the best that can be done with the method.”

States that Arnold's pptn. of BaSO_4 , *cold*, cannot be relied upon; that Blair's pptn. with 5 cc. conc. HCl gives results from 0.004 per cent. to 0.008 per cent. too low. A. boils $\frac{1}{2}$ hour and lets stand over night.

In 9 cases precipitation was complete.

34 cases filtrate contained 0.001 to 0.002 per cent. S.

11 cases filtrate contained 0.003 to 0.004 per cent. S.

8 cases filtrate contained 0.005 to 0.008 per cent. S.

∴ add 0.002 per cent. in all cases.

1901—CLASSEN, A. Book—"Ausgewählte Méthoden der Analytischen Chemie." F. Vieweg & Sohn, Braunschweig, 1901.

Pages 518 to 524 give methods for S in iron and steel.

1901—LINDSAY, W. G. *School of Mines Quarterly*, Vol. 23, p. 24. "On a Colorimetric Method for the Estimation of Sulphur in Pig Iron."

Also in: *J. Chem. Soc. Lond.*, (1902), p. 425.

J. Soc. Chem. Ind., (1902), p. 279.

J. I. S. I., Vol. 61, p. 469 (1902).

Central Blatt, (1902), p. 799.

From a 5-gram sample the H_2S liberated with HCl is absorbed in $NaOH$; a small portion of the solution is taken, acidified with H_2SO_4 and paraphenylenedimethyldiaminehydrochloride and $FeCl_3$ added; the color developed is compared with standards.

Sample	Elliott's method	Arnold's method	Bamber's method	Methylene blue			
A	0.025	0.062	0.0695	0.025	0.025	0.025	0.027
					av. = 0.025		
B	0.023	0.022	0.025	0.023	0.022	0.025	
					av. = 0.023		
C	0.0956	0.093	0.101	0.095	0.095	0.095	0.095
					av. = 0.095		

1901—NOYES, A. W., AND HELMAR, —. *J. Am. Chem. Soc.*, Vol. 23, p. 675. "The Determination of Sulphur in Iron and Steel."

Also in: *Rev. Am. Chem. Res.*, Vol. 7, p. 175 (1901).

Ztschr. anorg. Chem., Vol 32, p. 382 (1901).

J. Chem. Soc. Lond., (1901), p. 687.

J. Soc. Chem. Ind., (1901), p. 1143.

The Analyst, Vol. 27, p. 26 (1902).

Ztschr. anal. Chem., Vol. 41, p. 116 (1902).

Recommends oxidation with Br or with KClO_3 , HNO_3 and KBr; Fe is pptd. with NH_3 and S pptd. with BaCl_2 in filtrate. Use $\frac{3}{5}$ of wt. of BaSO_4 as correction to get per cent. S.

7 standardizing detns.:

	Present	Found
S-free iron + $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$	0.0056 0.012 0.129	0.0050 0.011 0.129
Steel No. 1 + $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$	0.016 0.234	0.016 0.211
Iron No. 1 + $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$	0.490 0.689	0.500 0.679

"The following determinations were made with different methods of solution followed by precipitation of the iron with ammonia and determination of the sulphuric acid in an aliquot part of the filtrate."

	I	II	III	IV	V
Iron No. 1.....	0.105 0.041 0.079 0.077 0.054	0.059 0.074 0.098 0.031 —	0.094 0.097 0.089 0.087 0.090	0.075 0.084 0.088 — —	0.097 0.095 0.095 — —

Blair evolution

0.044
0.049
0.044
0.042

Aq. reg. (Blair)

0.084 0.077
0.080 0.068
0.088 0.058
— —

	200 cc. H_2O , 8cc. Br		^{120 cc.} HNO_3 (1.20) + 1 gr. KBr + 7 grs. KClO_3	
	Sol. S.	Total S	Sol. S.	Total S.
Iron No. 1.....	0.097	—	0.084	—
	0.095	—	0.088	—
	0.095	—	0.091	—
	0.085	0.106	0.088	—
	0.093	0.117	0.093	0.120
	—	—	0.083	0.106
	—	—	0.099	0.116
	—	—	0.095	0.107
	0.068	0.091	0.088	0.099
	0.070	0.092	0.086	0.095

Iron No. 3.....	0.129	0.155	0.157	0.159
	0.129	0.148	0.155	0.159
Iron No. 4.....	0.113	0.144	0.142	0.149
	0.110	0.147	0.141	0.149
Iron No. 5.....	0.075	0.095	0.083	0.095
	0.077	0.094	0.079	0.089
Iron No. 6.....	0.026	—	—	—
	0.027	—	—	—
	0.026	—	—	—
	0.029	—	—	—
Iron No. 7.....	0.018	0.029	0.019	0.022
	0.017	0.025	0.014	0.025

S in residue varies from 0.015 per cent. to 0.037 per cent. with average of 0.023 per cent. when detd. by $\text{Br} + \text{H}_2\text{O}$ method; with $\text{HNO}_3 + \text{KBr}$ residue contains average of 0.012 per cent. S, or from 0.002 per cent. to 0.027 per cent.

"With iron of a given character, the sulphur in the residue will probably be found nearly uniform, so that the original solution can be precipitated at once with ammonia, without previous filtration, and a constant correction for the sulphur of the residue applied. When this is done, the method becomes, we think, more rapid than any gravimetric method now in use."

1901—BLAIR, A. A., AND SHIMER, P. W. *Trans. Am. Inst. Min. Engrs.*, Vol. 31, p. 748. "A Crystalline Sulphide in Pig Iron."

Description and pictures of C-S-Ti compound found in pig iron; the cpd. is insoluble in dil. HCl. The hexagonal scales analyze: Ti, 62.82 per cent.; S, 22.64 per cent.; C, 9.82 per cent.; Fe, 1.82 per cent.

1902—NASKE, T. *Stahl u. Eisen*, Vol. 22, pp. 333 and 1134. "Colorimetrische Methode zur Bestimmung des Schwefels im Roheisen," and "Beiträge zu der Analyse des Eisens."

Also in: *J. Chem. Soc. Lond.*, (1902), p. 562; (1903), p. 185.

The Analyst, Vol. 27, p. 206 (1902).

J. I. S. I., Vol. 61, p. 649 (1902).

Chem. Ztg., Vol. 26, p. 333.

Central Blatt, (1902), p. 1343.

Uses paradimethylphenylendiamine which forms colored tetramethylthyoninchloride; results not good. NaOH is not a good absorbent as Na_2S , NaHS and polysulfids are formed; air converts these partly to thiosulfate; some S goes to H_2SO_4 , some H_2S escapes; longer action of passing gases leaves only NaOH in flask. This method (of Lindsay and Naske) gives only qualitative test for S.

In second article says AsH_3 , PH_3 and SiH_4 all react with AgNO_3 and spoil Bischoff's titration method.

1902—BISCHOFF, FELIX. *Stahl u. Eisen*, Vol. 22, p. 719. "Beiträge zu der Analyse des Eisens."

On p. 727 gives greatest allowable deviations in accurate analyses:

% of component present	% C allow	% allow. As. Cu, P, S, Si.	% allow. Al, Cr, Mn Mo, Ni and W
0.000-0.008	0.002	0.001	0.002
0.008-0.015	0.002	0.002	0.003
0.015-0.025	0.002	0.002	0.003
0.025-0.050	0.003	0.003	0.004
0.050-0.075	0.003	0.004	0.006
0.075-0.100	0.004	0.004	0.006
0.100-0.125	0.004	0.005	0.007
0.125-0.150	0.005	0.006	0.007
0.150-0.175	0.005	0.006	0.008
0.175-0.200	0.006	0.007	0.009
0.200-0.250	0.007	0.008	0.011
0.250-0.300	0.008	0.009	0.013
0.300-0.350	0.009	0.010	0.015
0.350-0.400	0.010	0.012	0.017
0.400-0.450	0.011	0.014	0.019
0.450-0.500	0.012	0.016	0.021
0.500-0.600	0.013	0.019	0.025
0.600-0.700	0.015	0.022	0.029
0.700-0.800	0.017	0.025	0.033
0.800-0.900	0.019	0.028	0.037
0.900-1.000	0.020	0.030	0.040
more	2%	3%	4%

1902—BISCHOFF, FELIX. *Stahl u. Eisen*, Vol. 22, p. 754. "Beiträge zu der Analyse des Eisens."

On page 756 says Cu_2S remains behind in evol. method; 4 parts Cu holding back 1 part S.

Uses chlorine method dissolving in HCl and Cl with good results. This method given in Fresenius, *Quant. Chem. Anal.*, 6th Ed., pages 506 to 510 and 512 to 513.

Cut of apparatus for Cl method:

- a. Flask for dissolving sample in 1.095 HCl.
- b. Condenser to return HCl.
- c and d. Alkaline Pb solution.
- e. Granular KClO_3 and dil. HCl.
- f. NaOH or NaOCl.

This method gives $\frac{1}{3}$ higher S than $\text{CuCl}_2 + \text{NH}_4\text{Cl}$ method. Apparently rubber connections used.

1902—BISCHOFF, FELIX. *Stahl u. Eisen*, Vol. 22, p. 1136. "Beiträge zu der Analyse des Eisens."

Discusses evolution method with Naske. AsH_3 and PH_3 no influence as following results show:

Sample	Gravi.	Ag-titr.	Sample	Gravi.	Ag titr.
C_1	0.0570	0.0582	S_{22}	0.0420	0.0430
C_2	0.0263	0.0270	S_{24}	0.0670	0.0678
W_1	0.6600	0.6630	E_{10}	0.0186	0.0192
W_7	0.0550	0.0558	E_{11}	0.0212	0.0220
W_9	0.0738	0.0748	—	—	—

1902—BREARLEY, HARRY AND IBBOTSON, FRED. Book—"The Analysis of Steel Works Materials," 1902.

Elaborate review and discussion of S detn., beginning p. 37. Over 100 references to direct and related articles. No new data.

Page 42: "Some experiments by Matthewman (West of Scotland Iron and Steel Institute, Session 1895-96) elucidate a point in the evolution process which is rarely alluded to. He found that the sulphur evolved from pig iron and high carbon steel samples was greater the more rapid the evolution, and that the highest results were obtained when the rate of evolution was so rapid as almost to project the absorbing liquid from the vessel, and certainly so rapid that a portion of the sulphuretted hydrogen

escaped absorption. A pig iron containing 0.15 per cent. sulphur gave the following results: 0.132, 0.122, 0.092, 0.076, 0.049, 0.036."

1902—WALTERS, H. E., AND MILLER, R. *Proc. Eng. Soc. West. Penn.*, Vol. 18, p. 83. "An Accurate Estimation of Sulphur in Iron by the Evolution Method."

Also in: *The Analyst*, Vol. 27, p. 206 (1902).

J. I. S. I., Vol. 61, p. 651 (1902).

W. and M. anneal their samples before evolving H_2S ; they heat in porcelain or copper boat in porcelain or nickel tube in combustion furnace for 15 mins., 30 mins. if Ti is present. Use either natural gas or hydrogen to prevent oxidation. Complete with $CdCl_2$ absorption and iodine titration.

		Evolution	Anneal + evolution	Gravimetric	
A. F. A. Standard Iron B					
ev. S = 0.038%; ox. S = 0.056%		0.038	0.056	0.056	
		0.038	0.055	0.054	
		0.040	0.057	0.057	
A. F. A. Standard Iron C					
ev. S = 0.059%; ox. S = 0.076%		0.059	0.076	0.076	
		0.059	0.075	0.074	
		0.060	0.074	0.075	
Other samples	1	0.057	0.071	0.070	0.071
		0.057	0.071	0.071	0.071
	2	0.034	0.039	0.038	
		0.034	0.039	0.039	
	3	0.045	0.051	0.052	
		0.046	—	—	
	4	0.049	0.059	0.059	
	5	0.080	0.085	0.086	
		—	0.084	—	
	6	0.026	0.026	0.026	
	7	0.036	0.035	0.034	
	8	0.052	0.051	0.053	

1902—DOUGHERTY, GEO. T. *The Iron Age*, Vol. 69, p. 14.
 "Notes on Iron Analysis."

Refers to work of Walters and Miller and makes annealing more practical by use of filter paper and covered crucible, uses dil. acid.

A. F. A. Standard Iron B; ev. S = 0.038%, ox. S = 0.056%	
Not ignited	0.041%
Ignited 30 min. in paper.....	0.059
	0.053
Ignited 15 min. in paper.....	0.049
	0.052
Ignited without paper.....	0.055
	0.057
Ignited with paper on top.....	0.058
	0.057

A. F. A. Standard Iron C; ev. S = 0.059%, ox. S = 0.076%	
Without ignition	0.060%
Ignited 30 min. in paper.....	0.076
	0.076
Ignited 15 min., paper on top.....	0.079
	0.076

A. F. A. Standard Iron D; ev. S = 0.024%, ox. S = 0.031%	
Without ignition	0.022%
Ignited 15 min., paper on top.....	0.031
	0.031

Other samples of pig iron:

Sample	Oxidation	Evolution	Ignit. + evol.
1	0.046	0.020	0.043
2	0.032	0.010	0.030
3	0.011	0.003	0.009

1902—STEHMAN, J. V. R. *J. Am. Chem. Soc.*, Vol. 24, p. 644.
 "The Application of Eschka's Method to Pig Irons."

Also in: *The Analyst*, Vol. 27, p. 305 (1902).
J. Chem. Soc. Lond., (1902), p. 699.

Determines S in pig irons by Eschka's method; 50 mesh is the limit of coarseness that can be used.

Sample	Evolution + S in residue		KClO ₃ + HNO ₃		Bamber's		Eschka's	
Gray forge pig	0.035	0.036	0.036	0.035	0.035	0.036	0.039	0.0399
	0.036	0.035	0.035	—	0.034	0.035	0.039	0.0394
	—	—	—	—	0.036	—	0.040	0.0385
	—	—	—	—	—	—	0.042	—
Chilled basic pig	0.032	0.032	0.032	0.030	0.030	0.031	0.031	0.031
	0.032	—	0.030	0.032	—	—	0.032	—
A. F. A. Standard								
Sample C;								
ox. S = 0.076	0.066	—	0.075	0.075	0.076	—	0.077	0.076
	—	—	0.076	—	—	—	0.076	—
A. F. A. Standard								
Sample B;								
ox. S = 0.056	0.043	—	0.058	0.055	0.054	—	0.054	0.057
	—	—	0.058	—	—	—	0.056	0.043*
White iron	—	—	—	—	0.431	0.432	0.432	0.430
	—	—	—	—	0.429	—	0.430	—

*This on 30-mesh material.

1902—WENCELIUS, ALBERT. Book—"Methodes d'Analyse des Laboratoires d'Acieres Thomas." Béranger, Paris, 1902.

Page 48 gives Schulte-Frank's method with 1 cut.

1903—DICKSON, W. E. *J. Am. Found. Assn.*, 1903, June. "Loss of Sulphur in Borings of Cast Iron."

Also in: *Iron Trade Review*, Vol. 36, p. 61 (1903).

Cast iron samples show loss of S although steel samples are constant. Thinks loss due to slow oxidation of large surfaces exposed.

	Original	Present
Standard 1	0.053	0.042
2	0.051	0.047
3	0.040	0.028
4	0.056	0.031
5	0.057	0.041
A. F. A. Standard B.....	0.038	0.036
A. F. A. Standard C.....	0.059	0.048

1903—FIELD, HERBERT E. *J. Am. Found. Assn.*, Vol. 11, p. 137. "Standard Methods for Analyzing Iron."

Evolution and oxidation methods given in detail. 14 pages of details and modifications.

1903—Ireland, W. G. *Iron Trade Rev.*, Vol. 36, p. 69. "Cast Iron Sulphur Standards."

Claims S gets lower in irons on standing.

	% S	
From June 12 to Aug. 12	0.170	A. F. A. Standard B:
From June 12 to Aug. 20	0.160	
From June 12 to Aug. 26	0.160	Straight 0.038
From June 12 to Aug. 27	0.159	0.036
From June 12 to Aug. 29	0.157	Annealed 0.057
From June 12 to Sept. 24	0.152	0.059
From June 12 to Oct. 14	0.150	
From June 12 to Nov. 17	0.147	

On annealing sample jumps back to 0.169–0.171

Oxidation method also gives 0.172

1903—KLEINE, A. *Chem. Ztg.*, Vol. 27, p. 729. "Neuerungen im analytischen Arbeiten."

Also in: *J. Chem. Soc. Lond.*, (1903), p. 694.

Apparatus for evolution method: flask with internal condenser and no rubber connections. Flowing water is not used, but the upper chamber is filled for each determination. 70 cc. conc. HCl used and only small flame required.

1903—LORD, N. W. Book—"Notes on Metallurgical Analysis." Ohio State University, 2nd Ed., 1903. Pages 95–110 on S. detn. 3rd. Ed. appeared under authorship of Lord and Demorest in 1903, 4th Ed. in 1916.

1903—PROST, E. Book—"Manuel d'Analyse Chimique." Ch. Beranger, Paris, 1903. Pps. 309–311 on S detn. in iron and steel.

1903—SEYLER, C. A. *The Analyst*, Vol. 28, p. 97. "Note on the Estimation of Sulphur in Pig Iron."

Also in: *J. Chem. Soc. Lond.*, (1903), p. 450.

J. Soc. Chem. Ind., (1903), p. 573.

Measures temperature used in annealing and finds 750° C. best.

Uses conc. HCl; ignites sample at 750° for 15 mins.; employs red hot tube and H₂ with good results. KOH as

absorbent gives low results, especially without a condenser, and when it gets hot.

Results on 1 sample:

Bamber's method	0.174% S
Aq. reg. method	0.172
HCl, 1-1 (iodine)	0.111
Sample ignited	0.125
Sample ignited and conc. HCl.....	0.142
Ditto with H ₂	0.150
(0.02% S left in residue)	
H ₂ without condenser	0.124-0.136
H ₂ with condenser	0.14
Br. in HCl	0.138-0.143
Ditto with 15 min. ign.....at 700°	0.154
	at 750° 0.162
	at 800° 0.154

1904—CROBAUGH, F. L. Book—“*Methods of Chemical Analysis and Foundry Control.*” Pub. by author, Cleveland, Ohio, 1904.

Page 59 confirms findings of Dickson and of Ireland as to decrease of S as sample ages, also that annealing restores S content. Finds decomposition of H₂S if work is done in bright sunlight; the loss may amount to $\frac{1}{3}$ of total S. Uses evolution (iodine) method with anneal of sample.

First edition of book appeared in 1901.

1904—KNIGHT, S. S. *Iron and Steel Mag.*, Vol. 7, p. 486. “A Rapid Method for Determining Total Sulphur in Iron by Evolution.”

Also in: *Iron Age*, Feb. 25, 1904.

First anneals sample with pure iron dust then iodine-evol. method.

1904—DOUGHERTY, GEORGE T. *The Iron Age*, March 31, 1904. “The Total Sulphur and Different Forms of Sulphur in Pig and Cast Iron.”

Also in: *Rev. Am. Chem. Res.*, Vol. 10, p. 341 (1904).

Discusses annealing of sample and absorbents. New Jersey titaniferous pig may retain more insoluble than is evolved. Strong KOH is a better absorbent than amm. CdCl₂. Mentions his 3 forms of S in pig iron.

Number	Evolved	Residual	Evolved and residual	Annealed and evolved	Gravimetric
948	0.057	0.070	0.127	0.122	0.128
949	0.018	0.061	0.079	0.080	0.079
951	0.035	0.050	0.085	0.082	0.090
2423	0.038	0.045	0.083	0.072	—
2424	0.078	0.039	0.117	0.103	—
2425	0.063	0.033	0.096	0.085	—
2349	0.068	0.057	0.125	0.120	—
Sp. 1	0.008	0.027	0.035	0.034	—
		Average	0.093	0.087	

1904—FORD, ALLEN P., and WILLEY, ODGEN G. *J. Am. Chem. Soc.*, Vol. 26, p. 201. "The Determination of Sulphur in Iron."

State that works' chemists usually get quite accurate results, but that commercial chemists are apt to be low.

Consider evolution method adjunct to and dependent on the oxidation method.

Losses in oxidation method discussed, especially on solution:

Sample	With watch glass	Without glass
1 Gray cast iron.....	0.112% S	0.103% S
2 Gray cast iron.....	0.143	0.131
3 Gray cast iron.....	0.134	0.113
4 Gray cast iron.....	0.137	0.113
5 Bessemer pig	0.045	0.038
6 Bessemer pig	0.047	0.037
7 No. 2 Foundry.....	0.018	0.023
8 No. 2 Foundry.....	0.036	0.030
9 No. 2 Foundry.....	0.044	0.019
10 Bessemer steel.....	0.080	0.071
11 Bessemer steel.....	0.073	0.075

F. and W. disparage the recommendations of Noyes and Helmar and propose a shortened Bamber's method.

1904—MACPHERRAN, R. S. *Trans. Am. Found. Assn.*, June, 1904. "Sulphur in Pig Iron."

Discusses results on chill and sand castings and correction factors. "The average of 114 determinations of volatile and insoluble sulphur resulted as follows: volatile, 0.045; insoluble, 0.003. There seemed to be no connection

between the total and the insoluble, often the highest volatile giving the lowest insoluble and vice versa."

- 1904—FRICKE, L. *Stahl u. Eisen*, Vol. 24, p. 890. "Schwefelbestimmung im Roheisen und Stahl durch Titration mit Jod und Thiosulfatlösung."

Follows Kleine and Lunge; adds excess I_2 and back with $Na_2S_2O_3$.

- 1904—OLSEN, J. C. Book—"Quantitative Chemical Analysis." D. Van Nostrand, New York, 1904.

Pages 351-356 on S detn.; page 354 cut of evol. apparatus having rubber connections, outside air condenser and continued tube heated by flame.

- 1905—FURMAN, H. VAN F. Book—"A Manual of Practical Assaying." Wiley, New York, 5th Ed., 1905.

Page 88 gives methods for different materials.

Page 94 gives Karsten's $HCl-H_2SO_4$ method with cut.

Page 96 gives Morrell's iodine method.

- 1905—FRIEDHEIM, CARL. Book—"Leitfaden für die quantitative chemische Analyse." C. Habel, Berlin, 1905.

Page 527 gives evol. and color. methods, with cuts.

- 1905—KRUG, C. *Stahl u. Eisen*, Vol. 25, p. 887. "Eine Kritik der Schwefelbestimmung im Eisen."

Treats the iron chloride solution with silver oxide, this removes the iron as hydroxide and chlorine as silver chloride; the sulfuric acid is left and determined in filtrate. More rapid is ether separation of iron.

Sample	Bromine	Ether
Pig 1	0.165	0.183
	0.160	0.182
	—	0.183
	—	0.182
Pig 2	0.135	0.158
	0.133	0.156
Pig 3	0.410	0.441
	0.411	0.438
Steel 1	0.077	0.077
	0.077	0.078
Steel 2	0.065	0.067
	0.067	0.068

- 1905—McCABE, CHARLES R. *J. Am. Chem. Soc.*, Vol. 27, p. 1203.
 "Note on the Gravimetric Determination of Sulphur in Iron and Steel."

Notes on evol. and oxid. method. For oxid. method proposes a flask provided with long upright exit tube for gases. Quick evol. on foundry irons nearly agrees with oxid. method.

Sample	Iodine	Gravimetric
1	0.078	0.079
2	0.083	0.083
3	0.108	0.109
4	0.073	0.072

- 1905—PETRÉN, JACOB. *Jern-Kontoret Annaler*, Vol. 60, pp. 187-234. "Om bestämning af svafel uti järn."

Also in: *Stahl u. Eisen*, Vol. 26, p. 544 (1906).

A 47-page article with full discussion and innumerable references. Groups methods under (a) oxidation, (b) evolution, (c) halide solution. Gives rough table showing effect of HCl, NH_4Cl , NaCl and KCl on BaSO_4 .

Sample	BaSO_4 pptd. cold	HCl + KClO_3	Tamm's method
Gray iron	0.088	0.086	0.087
White iron	0.031	—	0.033
White iron	0.009	0.008	—
Steel	0.095	—	0.096
Basic steel	0.024	0.025	0.024

	Ledebur	Classen Lunge	HCl + H_2SO_4	HCl, 1.19	Wiborgh's	Actual
Gray iron	0.023	0.023	0.032	0.032	0.030	0.034
White iron	0.105	0.115	0.131	0.135	0.15	0.136
White iron	0.011	0.011	0.016	0.016	0.014	0.018
Steel	0.079	0.077	0.087	0.095	0.085	0.095
Steel	0.060	0.057	0.076	0.075	0.085	0.077
Basic steel	0.022	0.023	0.024	0.024	0.023	0.024
Wrought iron	0.033	0.033	0.006	0.006	0.0025	0.005

- 1905—PULSIFER, H. B. *Chemical News*, Vol. 90, p. 230. "A Radically New Method for the Determination of Sulphur in Irons and Steel."

Also in: *Rev. Am. Chem. Res.*, Vol. 11, p. 85 (1905).
Iron and Steel Mag., Vol. 8, p. 313 (1904).

Oxid. method dissolving in chloric acid. Residue is fused with Na_2O_2 and added to main soln. Method is so rapid that BaSO_4 can be pptd. in 20 mins. from weighing out sample.

Sample	S by rapid oxid.	S by slow oxid.	HClO_3 -soln., resid.		total
1	0.008	0.013	0.012	0.006	0.018
2	0.004	0.003	0.022	0.000	0.022
3	0.017	0.023	0.016	0.011	0.027
4	0.017	0.019	0.026	0.020	0.046
5	0.048	0.065	0.054	0.008	0.062
6	0.080	0.091	0.076	0.022	0.098
7	0.148	0.164	0.134	0.021	0.155

1906—McFARLANE, J., and GREGORY, A. W. *Chemical News*, Vol. 93, p. 201. "A modified Evolution Method for the Determination of Sulphur in Pig-Iron."

Anneals sample with cream of tartar in filter paper before regular evolution method. Finds only one absorption flask necessary.

Pig iron					"Chilled shot"			
Sample	Aq. reg.		Evolution		Sample	Aq. reg.		Evolution
1	0.093	—	0.090	0.089	1	0.186	0.188	0.190
2	0.090	0.090	0.091	0.094	2	0.197	0.204	—
3	0.096	0.098	0.093	0.095	3	0.129	0.129	—
4	0.066	0.066	0.066	0.068	4	0.115	0.113	—
5	0.078	0.080	0.080	0.080	5	0.086	0.085	0.087
6	0.060	0.060	0.060	0.061	6	0.148	0.152	—
7	0.063	0.063	0.062	0.061	7	0.222	0.222	—
8	0.076	—	0.078	0.078	Chilled samples			
9	0.069	0.068	0.069	0.070	1	0.448	0.440	0.438
10	0.082	—	0.080	0.080	2	0.292	0.285	0.282
					3	0.390	0.402	0.406
					4	0.476	0.458	0.464

1906—REINHARDT, C. *Stahl u. Eisen*, Vol. 26, p. 799. "Zur Bestimmung des Schwefels im Eisen mit besonderer Berücksichtigung des maassanalytischen Verfahrens."

A lengthy discussion (6 full pages) with many references. Gives cuts for apparatus, details of work and calculations. No new facts.

1906—Roos, J. O. *Kunigl. Tekniska Högskolans Materialprof-ningsanstalt*, 1896-1906, p. 34.

Also in: *Ztschr. anal. Chem.*, Vol. 45, p. 782 (1906).

Solubility of BaSO_4 :

Volume	HCl	BaCl_2	FeCl_2	BaSO_4 diss.
200 cc.	2.5%	1%	—	0.2 mg. at 18°
200 cc.	5-10%	1%	—	0.5 to 1.0 mg.
200 cc.	10 cc. 1.19	1%	15 grs.	0.5 mg.

Error due to solubility of BaSO_4 in actual solution cannot be over 0.002% and is more nearly around 0.001%.

1906—TREADWELL and HALL. Book—"Analytical Chemistry." Wiley, New York, 1st Ed., 1906.

Gives colorimetric, oxidation and evolution methods mixed in with other sorts of analyses.

1906—SCHULTE, WILHELM. *Stahl u. Eisen*, Vol. 26, p. 985. "Zur Bestimmung des Schwefels im Eisen."

Discovers that no organic S cpds. are formed if conc. HCl is used. 6 full pages of discussion with cut of evol. app. and results. No rubber used near flask.

Sample	Treatment	10 grs. Fe 66 cc. 1.19 HCl 132 cc. H_2O	10 grs. Fe 60 cc. 1.19 HCl 60 cc. H_2O	10 grs. Fe 50 cc. 1.19 HCl 0 cc. H_2O	10 grs. Fe 100 cc. HCl 1.19 0 cc. H_2O
English tool steel	Direct	0.0123	0.0182	0.0295	0.0299
	Red hot tube	0.0095	0.0076	0.0008	0.0004
	Total	0.0218	0.0258	0.0303	0.0303
Gray pig	Direct	0.0186	0.0210	0.0315	0.0331
	Red hot tube	0.0095	0.0094	0.0016	0.0004
	Total	0.0281	0.0304	0.0331	0.0335
File steel	Direct	0.0309	0.0380	0.0477	0.0517
	Red hot tube	0.0117	0.0105	0.0016	0.0008
	Total	0.0426	0.0485	0.0493	0.0525
Thomas pig	Direct	0.0630	0.0622	0.0735	0.0712
	Red hot tube	0.0101	0.0081	0.0024	0.0014
	Total	0.0731	0.0703	0.0759	0.0726
Iron	Direct	0.0825	0.0816	0.0792	0.0840
	Red hot tube	0.0048	0.0024	0.0016	0.0000
	Total	0.0873	0.0840	0.0808	0.0840
Mill pig	Direct	0.0970	0.1099	0.1083	0.1099
	Red hot tube	0.0065	0.0054	0.0016	0.0008
	Total	0.1035	0.1153	0.1099	0.1107

- 1907—ARNOLD and IBBOTSON. Book—"Steel Works Analysis. Whittaker & Co., London, 1907.

Pages 107-126 on S detn. Gives oxidation method and Arnold and Hardy's volumetric method. For absorption uses 14 tubes connected in series so that the blackening of each consecutive one containing the lead soln. means 0.01% S in sample.

- 1907—DUSSIER, EUGENE. *Stahl u. Eisen*, Vol. 27, p. 142. "Zur Bestimmung des Schwefels im Eisen."

Apparatus for evol. method. App. has condenser and special abs. bottle—no rubber connections.

- 1907—ORTHEY, MAX. Book—"Die Eisenhüttenchemie." Wilhelm Knapp, Halle, 1907.

Pages 142 to 159 give the 7 more important methods; good cut of Kleine's apparatus.

- 1907—ORTHEY, MAX. Book—"Laboratoriumsbuch für den Eisenhüttenchemiker."

Page 26, evolution method weighing as CuO. Nothing new.

- 1907—SIEDENER, C. F. Book—"Quantitative Metallurgical Analysis." H. W. Wilson Co., Minneapolis, 1907.

Pages 72-78 gives evol. color. and oxid. methods with cut of Wiborgh's app.

- 1907—NOSTITZ, VON, AND JANKENDÖRF. *Ztschr. anal. Chem.*, Vol. 46, p. 157. "Schwefelbestimmungsapparat."

Also in: *Chem. Abs.*, Vol. 1; p. 1088 (1907).

Describe and illustrate evol. flask with combined bulb-tube and sep. funnel above which serve as condenser and obviate rubber conn.

- 1908—AUCHY, G. *Chem. Eng.*, Vol. 7, p. 87. "Sulphuretted Hydrocarbon Loss in Evolution Methods for Sulphur in Steel and Cast Iron."

He has previously added 25 per cent. to evolution S to get equivalent of an oxidation method. "But to his horror and dismay his aqua regia result came 0.019 per cent. (0.026 reported). Hastily he repeated some of his old work that had been published. The results came as before. The truth then began to dawn on him. The truth is that this sulphuretted hydrogen loss is not, as he had supposed, an inevitable occurrence either in pig iron or high carbon steel. Nor on the other hand is it the case, as supposed by others, that the loss always occurs in pig irons, and never occurs in steels."

Sample	Evolution	Aqua regia
Washed metal	0.035	0.044
	0.021	0.019
	0.023	0.020
	0.023	0.021
Steel	0.025	0.027
	0.023	0.028
	0.023	0.023
	0.036	0.053
	0.062	0.084
	0.026	0.046
	0.037	0.067
	0.027	0.026

1908—BOLLING, R. *Eng. News*, Vol. 59, p. 505. "The Determination of Sulphur in Pig Iron and Steel by the Hydrogen Jet Method."

Also in: *Chem. Abstracts*, Vol. 2, p. 2351 (1908).

"The oxidation is so perfect in the hot hydrogen flame that no sulphur compounds escape complete oxidation; this accounts for the higher results obtained. In absorbing without special means some sulphur must escape. The novelty of the method outlined lies chiefly in the oxidation of the sulphur by the hydrogen jet and in the practical details, such as the combustion chamber, the ignition spark apparatus, the oxygen tube, etc. The method works best only under good laboratory conditions and in the hands of competent persons rather than amateurs."

Sample	Hydrogen jet	Evol.-CdCl ₂	Evol.-NaOH
Basic pig 741	0.0093	0.0084	0.0081
Basic pig 896	0.029	0.020	0.019
No. 1 foundry 1004.....	0.0250	0.0194	0.0190
Gray forge 1064.....	0.099	0.085	0.081
White iron 108.....	0.238	0.217	0.210
0.30 carbon steel 1246.....	0.044	0.040	0.041
0.55 carbon steel 2401.....	0.026	0.020	0.019
0.08 carbon steel 3090.....	0.050	0.049	0.046

The SO₂ is absorbed in Na₂CO₃ solution and either oxidized with KMnO₄ and pptd. as BaSO₄ or else the solution is acidified with HCl and titrated with iodine, using starch indicator.

1908—BOURREY AND MARQUET. Book—“*Traité d'Analyse Chimique.*” O. Doin, Paris, 1908.

Pages 263 to 266 to S detn. Several methods given; Rollet-Campredon's method given in detail with cut of apparatus.

1908—HEESS, J. K. Book—“*Practical Methods for the Iron and Steel Works Chemist.*” Chem. Pub. Co., Easton, Pa., 1908.

Iodine evol. and oxidation methods given briefly.

1908—ISHAM, HELEN, AND AUMER, JOSEPH. *J. Am. Chem. Soc.*, Vol. 30, p. 1236. “Direct Combustion of Steel for Carbon and Sulphur.”

Also in: *Chem. Abstracts*, Vol. 2, p. 3212 (1908).

“The results of this work show that with a basic protection, as powdered alumina, between the platinum of the crucible and the steel, some sulphur is retained by the burned steel, some by the alumina, and some is evolved in gaseous compounds. With an acid protection for the platinum, as powdered silica, one source of trouble is removed, and the sulphur is distributed between the iron residue and the evolved gases.”

1908—KINDER, H. *Stahl u. Eisen*, Vol. 28, pp. 249-254. “Schwefelbestimmung in Eisen und Stahl.”

This is the report of the chemists' committee to the German foundrymen's association.

It is found that quick evolution using conc. HCl gives highest results, even higher than can be obtained with heated tube and dil. acid. Details are given for oxidation of the H_2S with $BrHCl$ to weigh as $BaSO_4$ and to titrate pptd. CdS with iodine soln.

The most important results:

Sample of Steel, "C. S."				Sample of Steel, "C. S. W."			
HCl	H ₂ O	Time	% S	HCl	H ₂ O	Time	% S
100	200	45	0.139	100	200	1-45	0.106
100	200	50	0.140	100	200	2-30	0.059
100	200	55	0.136	100	100	1-15	0.109
100	200	1-30	0.124	100	100	1-45	0.084
100	200	1-35	0.119	100	50	1-05	0.124
100	100	45	0.133	100	50	1-30	0.102
100	100	45	0.134	100	0	60	0.125
100	100	55	0.133	100	0	1-55	0.121
100	100	1-15	0.130	Sample, "C. S."			
100	100	1-20	0.125				
100	50	45	0.144				
100	50	50	0.146	HCl	Titer	BaSO ₄	Red hot tube Titer BaSO ₄
100	50	1-10	0.143	1.19	0.137	0.140	0.138 0.141
100	50	1-25	0.141	2 : 1	0.135	0.135	0.137 0.137
100	0	50	0.146	1 : 2	0.127	0.124	0.130 0.129
100	0	1-00	0.146	Sample, "C. S. W."			
100	0	1-00	0.145				
100	0	1-25	0.145	1.19	0.122	0.111	0.123 0.113
				1 : 2	0.084	0.073	0.085 0.073
				Sample, Basic Pig			
				1.19	0.076	0.075	0.077 0.082
				1 : 2	0.053	0.058	0.058 0.067

1908—MEURICE, ALBERT. Book—"Cours D'Analyse Quantitative des Matieres Minerales." Dunot et Pinat, Paris, 1908.

Several methods given, pages 285-301; good cut of Schulte's app.

1908—NEUMANN, B. Book—"Post's Chemisch-Technische Analyse." F. Vieweg & Sohn, Braunschweig, 1908.

Several methods are given in Vol. 1, pp. 647-658; excellent cut of Schulte's apparatus with furnace given on page 653.

- 1908—ORTHEY, MAX. *Ztschr. angew. Chem.*, Vol. 21, p. 1359 and 1393. "Die Bestimmung des Schwefels im Eisen und Stahl."

A massive investigation demonstrating the advantage of conc. HCl for the evol. method; results show that the BaSO₄ method is not necessary for accurate work. S found insoluble in residues only 0.46 per cent. and may be neglected.

Table of results is given on double page.

- 1908—RAYMOND, E. *Bull soc. belg. chim.*, Vol. 22, p. 181. "Nouvelle disposition d'appareil pour le dosage du soufre dans les fontes et les aciers."

Also in: *Chemical Abstracts*, Vol. 3, p. 1951 (1909).

A glass apparatus allowing H₂S to be oxidized by Br; no rubber.

1908—ORTHEY, MAX.—(Continued)

Methods of Determining S	1	6	7	11	12	16	19	21	22	23
Assumed S content	0.027	0.125	0.193	0.125	0.168	0.134	0.074	0.042	0.056	0.038
(a) Eggertz colorimetric	0.02	0.15	0.20	0.15	0.20	0.15	0.08	0.06	0.06	0.04
(b) Wiborgh's colorimetric	0.04	0.13	0.16	0.12	0.15	0.15	0.08	0.05	0.06	0.04
(c) Evolution into Cd-soln.										
(1) Solution by 1:2 HCl.....	0.0224	0.1069	0.1604	0.1167	—	—	0.0713	0.0290	0.0400	—
(2) ditto, heating gases.....	0.0254	0.1124	0.1824	0.1236	—	—	0.0729	0.0345	0.0465	—
(3) Solution by 1:124 HCl.....	0.0234	0.1080	—	—	—	0.1250	—	0.0315	0.0412	—
(4) ditto, heating gases.....	0.0258	0.1130	—	—	—	0.1364	—	0.0356	0.0468	—
(5) Solution by 1:2 HCl and 1:4 H ₂ SO ₄	0.0239	0.1076	0.1703	—	0.1570	—	—	0.0320	—	0.0204
(6) ditto, heating gases.....	0.0260	0.1145	0.1854	—	0.1620	—	—	0.0367	—	0.0342
(7) Solution by 1:19 HCl.....	0.0263	0.1213	0.1900	0.1284	0.1645	0.1370	0.0742	0.0416	0.0534	0.0376
(8) ditto, heating gases.....	0.0268	0.1246	0.1935	—	—	—	—	0.0423	0.0545	0.0384
(9) ditto, heating gases and water trap..	0.0274	0.1260	0.1946	0.1291	0.1682	0.1372	0.0751	0.0435	0.0564	0.0390
(10) ditto, into Cd-Zn-acet. soln.....	0.0272	0.1254	0.1950	0.1284	—	—	0.0748	—	—	—
(11) ditto, into NH ₃ ; titrated.....	0.0272	0.1258	—	0.1286	0.1675	—	—	0.0439	0.0559	—
(12) ditto, titrated in C ₂ H ₃ O ₂ soln.....	0.0276	—	0.1940	—	—	0.1365	—	—	0.0552	—
(d) Oxidation of H ₂ S with H ₂ O ₂	0.0267	—	—	0.1292	—	—	—	0.0441	—	—
(e) Oxidation of S with HNO ₃	0.0274	0.1262	0.1917	0.1290	0.1684	0.1368	0.0752	0.0436	0.0559	—
(f) Solution in Cu(NH ₄)Cl ₂ soln.....	0.0270	0.1249	—	—	0.1676	—	—	0.0439	—	0.0356

- 1908—ROSENHAIN, W. *J. I. S. I.*, Vol. 76, p. 87. "The Metallurgical and Chemical Laboratories in the National Physical Laboratory."

The detn. of S is mentioned on page 102. Evolution and oxidation methods given with following results. Rather poor cut of apparatus used.

Sample	Evolution	Gravimetric
896	0.042	0.041
936	0.046	0.049
952	0.045	0.049
Shaft	0.041	0.043
969	0.014	0.013
980	0.048	0.045
1018	0.054	0.052
1054	0.062	0.063

- 1908—SZÁSZ, E. *Stahl u. Eisen*, Vol. 28, p. 1466. "Zur Bestimmung des Schwefels in Eisenorten."

Also in: *Chem. Abstracts*, Vol. 3, p. 1131 (1909).

Evolution method dissolving in conc. HCl and absorbing in soln. of Cd and Zn acetates and acetic acid; iodine titration. Cut of app. given. No condenser; rubber connections.

- 1909—JABOULAY, E. *Rev. gen. chim.*, Vol. 12, p. 190. "Dosage du soufre dans les aciers, fers et fonte."

Also in: *Chem. Abs.*, Vol. 4, p. 34 (1910).

Evol. method using conc. HCl, $\text{Zn}(\text{OAc})_2$ and I_2 titer. Cut of neat apparatus having internal condenser filled once for each detn. No rubber at flask.

- 1909—MACFARLANE, W. Book—"Laboratory Notes on Iron and Steel Analysis." Longmans Green & Co., London, 1909.

Evolution and oxidation methods given, pages 43-56; page 91 says to anneal white irons and also gives oxid. method. Cut of primitive app.

- 1909—MILLS, C. GORDON. *Iron Age*, Vol. 84, p. 1318. "Determining Sulphur in Steel."

Also in: *Chem. Abstracts*, Vol. 4, p. 2221 (1910).

Description and cuts of multiple app. for evol. method.
Dilute acid and rubber connections.

- 1909—PREUSS, G. *Ztschr. angew. Chem.*, Vol. 22, p. 2044. "Apparate zur Schwefelbestimmung in Eisen und Stahl."

Compact condensing app. for conc. HCl and without rubber. No. 2 form is best adapted to catch all HCl.

- 1909—PREUSS, G. *Stahl u. Eisen*, Vol. 29, p. 1444. "Apparate zur Schwefelbestimmung in Eisen und Stahl."

Other designs of evolution apparatus.

- 1909—SCHMIDT, ALFRED. *Stahl u. Eisen*, Vol. 29, p. 1278. "Schwefelbestimmung im Eisen."

Also in: *Chem. Abstracts*, Vol. 5, p. 649 (1911).

Compact app. for evol. method. CO₂ is generated to sweep out last of H₂S by adding bicarbonate soln. to flask. One unit contains condenser, absorption vessel, wash gas generator; no rubber. Results:

Pig material	Schulte's	CdS-CuO	Official	New app.
245	0.089	0.095	—	0.103
247	0.030	0.031	—	0.031
248	0.121	0.121	—	0.125
250	0.040	—	—	0.040
251	0.079	0.095	—	—
252	0.079	—	—	0.080
253	0.088	0.089	—	0.097
254	0.085	0.070	—	0.097
267	—	0.091	—	0.098
286	—	—	0.091	0.091
287	—	—	0.088	0.084

- 1909—SCHOTT, E. A. *Stahl u. Eisen*, Vol. 29, p. 1444. "Neuer Kolben zur Bestimmung von Schwefel und Kohlenstoff."

Compact apparatus with condenser, wash connections, and feed bulb; no rubber and all in 1 piece. Cut of apparatus.

- 1910—HILLEBRAND, W. F. "*The Analysis of Silicate and Carbonate Rocks.*" U. S. Geological Survey, Bulletin 422, 1910.

Page 193 discusses the detn. of S in different materials and by several methods. References given.

- 1910—LUNGE and BERL. Book—“*Chemisch-technische Untersuchungsmethoden.*” J. Springer, Berlin, 6th Ed., 1910.

Pages 511-518 on detn. of S; several methods and cuts.

- 1910—TRAUTMAN, W. *Ztschr. anal. Chem.*, Vol. 49, p. 360. “Schwefelbestimmung in Molybdän- und Wolfram-Metall und in deren Eisenlegierungen.”

Also in: *Chem. Abstracts*, Vol. 4, p. 1953 (1910).

Direct combustion of fine powder in porcelain boat with oxygen in furnace absorbing gases in KOH and oxidizing to weigh as BaSO_4 .

- 1910—ANON. *Chem. Ztg.*, Vol. 34, p. 231. “Ein vereinfachter Apparat zur Bestimmung des Schwefels im Eisen nach Jenner.”

A combined condenser and safety tube to be fitted to flask; no rubber at flask.

- 1910—KINDER, H. *Stahl u. Eisen*, Vol. 31, p. 1838. “Ueber die Schwefelbestimmung in Roheisen und Stahl.”

Also in: *Chem. Abstracts*, Vol. 6, p. 969 (1912).

Since an iodine soln. is not permanent a KMnO_4 soln. is used to liberate an excess of free iodine; some reacting with the CdS the excess is titrated with thio. The iodine put in play thus depends only on the KMnO_4 and thio solns.

Sample	Gravimetric	Above method	Usual iodine
1	0.140	0.139	0.137
	0.141	0.139	0.138
	—	0.137	—
	—	0.140	—
2	0.123	0.126	0.122
	—	0.126	0.123
	—	0.129	—

- 1910—MULLER, ERICH, and DIETHELM, BERNARDO. *Ztschr. angew. Chem.*, Vol. 23, p. 2114. “Die Bestimmung des Kohlenstoffs und Schwefels in den hochprozentigen Le-

gierungen des Wolframs, Molybdäns und Vanadiums mit Eisen."

Also in: *Chem. Abstracts*, Vol. 5, p. 649 (1911).

Direct oxidation by combustion at 1100° with PbO_2 in porcelain boat in electric furnace. After 15 mins. for reaction the PbO_2 is boiled with Na_2CO_3 and S detd. in aliquot part. This method gives higher results than solution in acids. Many references.

1910—KLEINE, A. *Chem. Ztg.*, Vol. 34, p. 636. "Neue Apparate zur Schwefel und Arsen-Bestimmung."

Also in: *Chem. Abstracts*, Vol. 4, p. 3024 (1910).

Units with condensers and no rubber connections for evol. method.

1910—PREUSS, G. *Ztschr. angew. Chem.*, Vol. 23, p. 1980. "Apparate zur Bestimmung des Kohlenstoffs, Arsens und Schwefels in Eisen und Stahl."

Compact apparatus without rubber connections to use and condense conc. HCl for evol. method. The water in condenser may preferably be a bicarbonate soln. which is finally run into flask to sweep out last of H_2S .

1910—PREUSS, G. *Chem. Ztg.*, Vol. 34, p. 840. "Neuer Schwefelbestimmungs-apparat."

Also in: *Chem. Abstracts*, Vol. 4, p. 3024.

Wide-mouthed evolution flask with condenser, previous app. simplified; no rubber.

1910—PREUSS, G. *Ztschr. angew. Chem.*, Vol. 23, p. 250. "Apparate zur Schwefelbestimmung in Eisen und Stahl."

Diagrams of improved app. without rubber for evol. method with following results:

	I	2	3	4	5
Former app.	0.041	0.056	0.069	0.048	0.124
New app.	0.039	0.053	0.070	0.044	0.123
	0.040	0.055	0.069	0.047	0.126

1910—RÜDISÜLE, A. Book—"Die untersuchungsmethoden des Eisens und Stahls." Max Drechsel, Bern, 1910.

Pages 1-48 on detn. of S; 175 references on subject; an uncritical compilation without cuts or results. Brief outlines of methods which are arranged in 6 groups. All references have been included in present list.

- 1911—ELLIOTT, T. GIFFORD. *J. I. S. I.*, Vol. 83, p. 412. "The Volumetric Estimation of Sulphur in Iron and Steel."

Also in: *Chemical News*, Vol. 104, p. 298.

Iron Coal Trades Rev., Vol. 82, p. 760.

Chemical Abstracts, Vol. 5, p. 2789 (1911).

Anneals 5 grs. sample with 0.25 gr. ferrocyanide for 20 mins. at 750°-850° in a closed muffle. Completes evol. method using conc. HCl, condensing tube, CdCl₂ soln. iodine in excess and titer with hypo standardized against iron of known S content.

Sample	Gravimetric	No. ann.	700°	750°	800°	850°	900°	950° + paper burnt off
Steel	0.061	0.025	0.046	0.058	0.061	0.059	0.053	0.046
		0.026	0.045	0.058	0.060	0.059	0.054	0.051
Special								
Steel	0.051	0.030	0.045	0.049	0.051	0.050	0.048	0.050
		0.031	0.048	0.050	0.051	0.047	0.046	—
Steel	0.054	0.053	—	—	0.053	—	0.048	0.054
		—	—	—	0.054	—	—	0.055
Iron	0.085	0.085	0.083	0.085	0.084	0.080	0.066	0.084
		0.086	0.087	—	0.085	0.081	0.071	—
Iron	0.053	0.028	—	0.052	0.051	0.048	—	0.051

- 1911—GIOLITTI, F., and MARCANTONIO, M. *Rass. min.*, Vol. 35, p. 67.

Also in: *Chemical Abstracts*, Vol. 5, p. 3548 (1911).

Modifies Arnold and Hardy's method by using heated tube; special bulbs contain Pb or Cd acet. soln. Results reported from 0.001% to 0.004% lower than by oxidation method.

- 1911—KEELER, WARREN I. *Iron Age*, Vol. 86, p. 492. "A Modification of the Oxidation Method for Determining Sulphur."

Also in: *Chemical Abstracts*, Vol. 5, p. 3548 (1911).

Oxidation method modifying by addition of HF for ferroalloys.

Results:

Blank	0.001%	Bess. steel (0.060 stand.)	0.060%
Cabon iron	0.005		0.061
	0.006	Cast iron (0.034 stand.)	0.034
Dora iron	0.023		0.034
	0.023	Cruc. steel (0.020 stand.)	0.019
O. H. steel.....	0.057		0.020
	0.059	Chrom-tung-mol. steel...	0.008
Chrom-tung. steel.....	0.012		0.008
Ferrosilicon	0.022	White iron (0.250 stand.)	0.250
Ferrochrome	0.007		0.247
			0.246

1911—WENNMANN, D. *Chem. Ztg.*, Vol. 35, p. 596. "Neuer Schwefelbestimmungsapparat."

Also in: *Chemical Abstracts*, Vol. 5, p. 2991 (1911).

Special apparatus for evol. method with condenser and without rubber; cut.

1911—WENNMANN, D. A. *Chem. Ztg.*, Vol. 35, p. 863. "Apparate zur Schwefelbestimmung in Eisen und Stahl."

Also in: *Chemical Abstracts*, Vol. 6, p. 1 (1912).

Special apparatus of evol. method; no rubber; cut.

1911—WENNMANN, D. A. *Ztschr. angew. Chem.*, Vol. 24, p. 1861. "Neue Apparate zur Schwefel- und Kohlenstoffbestimmung in Eisen und Stahl."

Also in: *Chemical Abstracts*, Vol. 6, p. 1 (1912).

Special apparatus for evol. method; no rubber; cut.

1911—ANON. *U. S. Bureau of Standards Circular*. "Analyzed Irons and Steels—Methods of Analysis." Department of Commerce and Labor, 2nd Ed., 1911.

Gives HNO_3 oxid. method with fusion of residue; also evol. method with absorption in H_2O_2 and weighing as BaSO_4 .

1912—BAUER and DEISS. Book—"Probenahme und Analyse von Eisen und Stahl." Julius Springer, Berlin, 1912.

Excellent on segregation of elements in materials and sampling. Gives evol., oxid. and fusion methods for S.

- 1912—BRANDT, L. *Stahl u. Eisen*, Vol. 31, p. 1935. "Zur Schwefelbestimmung in Eisen und Stahl."

Also in: *Chemical Abstracts*, Vol. 6, p. 2900 (1912).

Peculiar absorption vessels for evol. method; cut.

- 1912—CAMP, J. M. *J. Ind. Eng. Chem.*, Vol. 4, p. 801. "The Methods of the United States Steel Corporation for the Commercial Sampling and Analysis of Pig Iron." Chemists' Committee Report.

Evolution and oxidation methods given.

- 1912—KRUG, CARL. Book—"Die Praxis des Eisenhüttenchemikers." J. Springer, Berlin, 1912.

Pages 113 to 125 on S detn.; gives many methods without data. Three cuts of app. given; one for evol. method has no rubber connections.

- 1912—SPANG. *Chem. Ztg.*, Vol. 36, p. 392. "Vereinfachter Apparat zur Bestimmung des Schwefels in Eisen und Stahl."

Also in: *Chemical Abstracts*, Vol. 6, p. 1693 (1912).

Special apparatus for evol. method; condenser; no rubber at flask.

- 1912—VITA, A., and MASSENEZ, C. *Stahl u. Eisen*, Vol. 32, p. 2089. "Eine neue Schwefelbestimmung in Roheisen und Stahl."

Also in: *Chemical Abstracts*, Vol. 7, p. 1685 (1913).

Stahl u. Eisen, Vol. 32, p. 2089.

Evolution method titrating CdS direct with KMnO_4 in weak H_2SO_4 soln.; to restrain as much HCl as possible a special wash head is used on flask.

Sample	Gravimetric	New method	
		CdS boiled	CdS not boiled
Pig iron 1	0.244	0.243	—
2	0.203	0.206	—
3	0.132	0.133	—
4	0.113	0.114	—
5	0.085	0.087	—
6	0.064	0.066	—
7	0.045	0.049	—
8	0.044	0.051	—
Steel 9	0.048	0.048	0.051
10	0.040	0.045	0.042
11	0.043	0.044	0.041
12	0.030	0.035	0.035
13	0.031	0.033	0.027
14	0.027	0.029	0.026
15	0.021	0.023	0.020

1913—BECKURTS, H. Book—“*Die Methoden der Massanalyse.*”
F. Vieweg & Sohn, Braunschweig, 1913.

Page 298 gives method for detn. of H_2S and a couple of pages to H_2S from iron and steel. One cut.

1913—CLARK, W. W. *Met. Chem. Eng.*, Vol. 11, p. 256. “The Determination of Sulphur in Ferrovandium.”

Also in: *Chemical Abstracts*, Vol. 7, p. 2367 (1913).

“Evolution methods give low results, only 10% to 80% S being evolved. Conditions for $BaCrO_4$ method are not easily controlled. The old gravimetric method, in which S is weighed as $BaSO_4$, is very accurate, checking to 0.005%. Six detns. run concurrently by the detailed procedure do not require more than three hours actual work.”

1913—FISCHER, HANNS. *Chem. Ztg.*, Vol. 37, p. 1223. “Eine Abänderung des Schulteschen Schwefelbestimmungsapparat für Roheisen und Stahl.”

App. for evol. method with extra safety tube. Air may or may not be sucked through to sweep out H_2S . Cut and few results:

	Without air	Air for 5 mins.
I39B	0.012	0.011
I292	0.024	0.024
I40B	0.010	0.010
I297	0.018	0.017
I45B	0.017	0.017
I298	0.035	0.034
I301	0.028	0.034 0.029
I305	0.040	0.038
I309	0.061	0.062
I57B	0.031	0.030
I310	0.076	0.079
I99B	0.020	0.0205

1913—FRANKLIN, F. H. *J. Ind. Eng. Chem.*, Vol. 5, p. 839. "A Fusion Method for the Determination of Sulfur in Iron and Steel."

Dissolves the sample in copper-potassium chloride containing barium chloride, fuses insoluble residue with sodium carbonate and peroxide; acidifies water extract with hydrochloric acid, boils, evaporates and bakes; dissolves in dil. hydrochloric acid, filters, dilutes and ppts. BaSO_4 .

Results:

Sample	% S	Fusion method	Other methods
Bureau Standards C ren.	0.035	0.039	0.032g
B	0.039	0.038	0.042g
B	0.039	0.044	0.036v
B	0.039	0.041	—
C 2nd	0.034	0.032	—
C 2nd	0.034	0.036	—
C 2nd	0.034	0.043	—
D 3rd	0.035	0.036	0.041g
D 3rd	0.035	0.041	0.036v
0.4 Bess.	0.118	0.124	0.115g
Am. Found. Ass., A	0.056	0.057	—
Cupola iron 38676		0.177	0.155v
21678		0.123	0.113v
37485		0.108	0.105v
39991		0.102	0.097v
39345		0.160	0.130v
34245		0.116	0.101v
40103		0.165	0.147v
16519		0.128	0.105v
16450		0.124	0.107v

Sample	% S	Fusion method	Other methods
I6419		0.126	0.119g
30253		0.095	0.092v
I6519		0.128	0.116g
41173		0.131	0.096v
39345		0.170	0.130v
Pig irons (Cu = 0.76%)		0.054	0.054g
30402		0.053	0.040v
29765		0.075	0.074g
29949		0.047	0.047v
29949		0.051	—
2789		0.095	0.084g
I8169		0.049	0.044g
Chilled roll (white)		0.170	0.160g
Malleable as cast, 41652		0.148	0.095v
Malleable as cast, 41780		0.168	0.128v
Low S steel		0.014	0.010g

	Fusion	Volumetric	In filt. after 4 days
Sample 47006	0.136	0.114	0.0014 gr.
Sample 47007	0.121	0.109	0.0050 gr.
Sample 47008	lost	0.106	0.0025 gr.

	(100 cc. vol.)			
Solubility of BaSO ₄ in dil. HCl	0.25 cc.	0.50 cc.	1.00 cc.	2.00 cc.
Theoretical BaSO ₄		Found		
0.0294	0.0303	0.0304	0.0290	0.0312

1913—LORD and DEMOREST. Book—“*Metallurgical Analysis.*” McGraw-Hill Book Co., New York, 1913. Fourth Ed. in 1916.

Pages 93-108 on detn. of S in iron and steel. Gives oxidation and evolution methods with references and discussion. For evolution method uses conc. HCl and apparatus with rubber connections.

1913—PREUSS, G. *Chem. Ztg.*, Vol. 37, p. 82. “Apparat zur Schwefelbestimmung in Stahl und Eisen.”

Also in: *Chemical Abstracts*, Vol. 7, p. 1639 (1913).

“A cylindrical washer half filled with H₂O serves as a stopper for the evolution flask, the gases passing up through a spiral then down a central tube nearly to the bottom of the washer. Conc. HCl may be used.” Apparatus is simplification of previous models.

- 1913—VITA and MASSENEZ. Book—“*Chemische Untersuchungsmethoden für Eisenhütten und deren Nebenbetriebe.*” J. Springer, Berlin, 1913.

Pages 74-79 give 5 methods without cuts or data.

- 1913—GRANT. *Chem. Analyst*, Vol. 9, p. 9.

Also in: *Chemical Abstracts*, Vol. 8, p. 2325 (1914).

Evolution method, receiving H_2S on soln. of $Cu(NO_3)_2$ and estimating by color produced.

- 1914—JOHNSON, CHARLES MORRIS. Book—“*Rapid Methods for the Chemical Analysis of the Special Steels, Steel-Making Alloys, Their Ores and Graphite.*” Wiley & Sons, New York, 1920 (3rd Ed.).

States that evol. method gives low results on most materials. Recommends annealing sample or oxidation or fusion methods. Another device to get all S by evolution method is to ignite residue in current of H_2 and HCl and add H_2S thus won to that first obtained. Asserts that titanium and copper in steels make results by evol. method low.

- 1914—MISSON, G. *J. I. S. I.*, Vol. 89, p. 510 (May, 1914). “The Colorimetric Estimation of Sulphur in Pig Iron and Steels.”

States that previous colorimetric methods have had errors because—(a) too small sample taken; (b) too dil. acid used not all S evolved; they have also not been applicable to pig irons. M. uses 1 gr. sample and HCl, sp. gr. 1.14 treating in a small cup and catching H_2S with paper moistened with As_2O_3 in HCl reading amount of S by yellow coloration of paper. Cut of app.

	Sample	New method	Evol S	Gravi. S		Sample	New method	Evol. S	Grav. S
Steel	9057	0.07	0.07	0.065	Pigs (Basic)	0.15	0.146	0.162	
	9072	0.032	0.03	0.028		0.06	0.06	0.065	
	9256	0.048	0.046	0.045		0.108	0.098	0.107	
	9295	0.035	0.036	0.037		0.086	0.08	0.082	
	396	0.048	0.05	0.043		0.074	0.07	0.08	
	72	0.027	0.028	0.023		0.09	0.095	0.086	

Sample	New method	Evol. S	Gravi. S	Sample	New method	Evol. S	Grav. S
565	0.038	0.04	0.038		0.09	0.082	0.082
374	0.04	0.04	0.038		0.078	0.07	0.07
613	0.025	0.03	0.026		0.098	0.098	0.097
650	0.047	0.044	0.049		0.09	0.09	0.098
665	0.04	0.038	0.037		0.08	0.076	0.082
741	0.048	0.046	0.05		0.145	0.15	0.154
34	0.028	0.026	0.026		0.098	0.092	0.094
821	0.033	0.036	0.036	1342	0.084	0.08	0.08
					0.12	0.115	0.122
					0.12	0.124	0.122
				(Bessemer)	0.02	0.018	0.026
					0.034	0.034	0.037
					0.038	0.04	0.041
					0.03	0.03	0.031

1915—BAUER, O., and DEISS, E. Book—“*The Sampling and Chemical Analysis of Iron and Steel.*” McGraw-Hill Book Company, New York, 1915. Translated by Hall and Williams.

This authorized translation of the German text has the same splendid features explaining the structure of materials while the chemical methods have been elaborated and brought more up-to-date by the translators. The first part of the book deals with segregation of the elements in steel products; the structures are abundantly and clearly illustrated so that the foundation is built for proper sampling and the reason for non-uniform samples and variation in chemical results made clear.

Pages 250 to 262 are given to the determination of S in the ferrous materials. Six methods are given with many notes and about a dozen references.

1915—OSANN, BERNARD. Book—“*Leitfaden für Giessereilaboratorien.*” J. Springer, Berlin, 1915.

Gives a few methods for S detn.

1915—PHILLIPS, FRANCIS C. Book—“*Methods for the Analysis of Ores, Pig Iron and Steel in Use at the Laboratories of Iron and Steel Works in the Region about Pittsburgh.*” The Chemical Pub. Co., Easton, Pa., 2nd Ed., reprint, 1915.

States those modifications of the standard methods which the several laboratories use.

- 1915—WHITE, CHARLES H. Book—“*Methods in Metallurgical Analysis.*” D. Van Nostrand Co., New York, 1915.

States necessity for correct sampling, but fails to follow with adequate directions. Oxidation and evol. methods given.

- 1916—PULSIFER, H. B. *J. Ind. Eng. Chem.*, Vol. 8, p. 1115. “The Determination of Sulfur in Iron and Steel.”

The study has a bibliography of 285 articles on S detn., classification of methods, study of the precision of results, 238 results on 22 samples by 3 methods, a short series to test the solubility of BaSO_4 in FeCl_3 solns. of different acidity, and details of the chloric acid method. See text for results.

- 1916—ZSCHIEGNER, HERBERT. *J. Ind. Eng. Chem.*, Vol. 8, p. 324. “An Accurate End-Point in the Volumetric Determination of Sulfur in Steel.”

Evol. iodine titration method with standardized details. Titrates in white porcelain beaker with 2 cm. black spot in bottom; end-point is when spot vanishes, regardless of the shade of blue of the solution.

- 1917—HILLEBRAND, W. F. *J. Ind. Eng. Chem.*, Vol. 9, p. 170. “Our Analytical Chemistry and its Future.”

Page 173.—“(2) The so-called evolution method for determining sulfur in iron and steel is one very much in vogue in industrial laboratories because of the short time required for the determination. In it the sulfur is driven out, mainly in the form of hydrogen sulfide, by boiling the alloy with hydrochloric acid, and collected in a solution of a cadmium salt with a view to determining the sulfur by titration with iodine. The method suffers, however, from defects, some of which are understood but others not, as is evidenced by the very discordant results that are reported by different analysts upon the same sample. So far as can

be determined, the most discordant results are sometimes obtained by analysts who seem to follow precisely the same procedure. Evidently there is room here for some critical research."

- 1917—FAY, HENRY. Book—"Quantitative Analysis." John Wiley & Sons, New York, 1917.

Pages 83 to 89 give evolution and Bamber's method with copious notes.

- 1917—SCOTT, WILFRED W. Book—"Standard Methods of Chemical Analysis." D. Van Nostrand, New York, 1917.

Evolution and oxidation methods briefly given on pages 229 to 231 and pages 398 to 403 give the evolution method in more detail. S. uses dil. HCl and rubber connections with special apparatus of his own design.

- 1918—BLAIR, A. A. Book—"The Chemical Analysis of Iron." J. B. Lippincott Company, Philadelphia, 8th Ed., 1918.

Since 1888 this book has been the standard text in America. In the 8th edition, pages 55 to 68 are devoted to sulfur; evolution, oxidation and fusion methods are given with notes and references.

- 1918—BROOKS, H. E. *Chem. Analyst*, Vol. 27, p. 9 (1918). Starch Indicator Solution.

Also in: *Chem. Abstracts*, Vol. 13, p. 1290 (1919).

"In detg. S is iron and steel by the evolution method, red color end points in the I titration are avoided by using an alk. soln. of sol. starch. Mix 10 g. sol. starch with 50 cc. cold H₂O, add 5 g. NaOH dissolved in 10 cc. H₂O and stir until a clear, viscous liquid is obtained. Continue stirring and slowly add 450 cc. cold H₂O. Use 2 cc. for each titration with I. A soln. prepd. in this way has been kept for 4 months without deterioration or loss of sensitiveness."

- 1918—LAISTER, C. P. *The Iron Age*, Vol. CI, p. 1093. "Determination of Sulphur in Alloy Steels."

As usual evol. method gives low results on alloy steels. L. dissolves in 100 cc. conc. HCl to which has been added

2.5 grs. KCl.; absorbs in KOH and titrates with iodine. The addition of the KCl hastens the reaction and makes results more satisfactory.

- 1918—PINSL, H. *Chem. Zeitung*, Vol. 42, pp. 369-371. Determination of Sulfur in Iron and Steel.

Also in: *J. Soc. Chem. Ind.*, Vol. 37, p. 422A.

Chem. Abstracts, Vol. 12, p. 2295.

"The H_2S evolved when Fe is treated with HCl may be absorbed in 5 per cent. NaOH soln.; the absorption is complete if the alkali soln. is contd. in a vessel 19 cm. high by 20 mm. wide. The sulfide is then detd. by pptn. as CuS after the alk. soln. has been neutralized, or it may be titrated iodometrically."

- 1918—PULSIFER, H. B. *J. Ind. Eng. Chem.*, Vol. 10, p. 545. "A Standard Apparatus for the Determination of Sulfur in Iron and Steel by the Evolution Method."

Describes a compact unit with internal condenser and ground joints for evol. method. Over 300 detns. are made on samples previously run by other methods, this time using conc. HCl and, in general, getting higher results. See text for figures and results.

- 1919—ANON. *Rass. min. met. chim.*, 49, 29-32. Unification of methods of analysis for iron and steel.

Also in: *Chem. Abstracts*, Vol. 13, p. 1570 (1919).

"Marinot, director of the steel works at St. Denis, advocates the following methods for cast irons and steels. Sulfur: Method of Rollet-Campredon, based on the formation of sulfur chloride and its subsequent reduction to H_2S in a quartz tube by H_2 in the presence of CO_2 . The H_2S is absorbed in a soln. of Zn acetate, and the ZnS detd. by titration with I."

- 1919—GOLDENBERG, LOUIS A. *Chem. and Met. Eng.*, Vol. 21, p. 628. "Determination of Sulphur and Chromium in Steel."

Evolution method using H_2SO_4 instead of HCl. 3-grm. sample is put in 500 cc. Erlenmeyer flask, rubber stopper,

CdCl_2 soln. to absorb H_2S which it titrated with KIO_3 in KI soln. Standardization is by known S steel.

1919—MAHLIE, W. S. *The Chemist Analyst*, Vol. —, p. 23. "A Method of Finding 'Blank' and Value of Iodine Solution in the Titration of Sulfur in Iron and Steel."

"In the volumetric determination of sulphur in iron and steel by standard iodine solution, a 'blank' must always be run, to find the amount of iodine required or consumed by the reagents and which must be subtracted from the total amount of iodine used.

"When the iron or steel is dissolved in hydrochloric acid there is an addition to the H_2S liberated (and also the large amount of hydrogen) some hydrocarbon gases, possibly some mercaptans and ferric chloride. In the determination of the blank by ordinary methods it is usually done by simply taking the usual amounts of absorbing reagent, indicator, etc., and titrating to the proper endpoint. It will readily be seen that this method does not take into consideration the probable effect of the above named gases.

"The following scheme has been used by the writer for a number of years and gives very good results.

"Two samples of steel are taken which have been made by the same process and are as nearly alike as possible with the exception of the sulphur content and the sulphur is evolved and titrated as in the ordinary method. Then a simple algebraic equation is used and the values for the blank and standard solution are calculated. The following example will make this clear.

"5 gms. steel containing 0.030 per cent. sulphur required 3.0 cc. iodine solution.

"5 gms. steel containing 0.044 per cent. sulphur required 5.0 cc. iodine solution.

"Then let y = blank in cc. x = value of iodine per cc.

$$\frac{.030}{x} + y = 3.6 \text{ cc.}$$

$$\frac{.044}{x} + y = 5.0 \text{ cc.}$$

$$\text{then } \frac{.014}{x} = 1.4 \text{ cc.}$$

$x = 0.010$ per cent. sulphur per cc.

$3.6 \text{ cc.} = 0.030 + y.$

$y = 0.6 \text{ cc. blank.}$ Columbus, O."

- 1919—MARINOT, A. *Am. chim. anal. chim. appl.*, Vol. 1, p. 153.
"Rapid Determination of Sulfur in Iron and Steel."

Also in: *Chem. Abstracts*, Vol. 13, p. 1682 (1919).

Dissolves 5 grs. sample in 60 cc. HCl (1-3) and 30 cc. H_2SO_4 (1-2) and evolves through condenser and wash bottle into ZnAc soln. Oxid. ZnS with excess I_2 and back titer with thio. Method cannot be used in presence of Cu or Mo.

- 1919—PHILLIPS, H. JOSHUA. *The Iron Age*, Vol. 103, p. 957.
"Simple Sulphur Extractor."

Also in: *Chem. Abstracts*, Vol. 13, p. 1269 (1919).

Iodine-evol. method dissolving in 160 cc. 1-5 H_2SO_4 and absorbing in NaOH; evidently rubber cork used. Cut of apparatus (Neutroscope).

- 1919—MOLYNEAUX, M. *Chem. Trade J.*, Vol. 65, p. 146. "Sulfur Estimation in Iron and Steel."

Also in: *Chem. Abstracts*, Vol. 13, p. 2649 (1919).

Adaptation of Phillips' neutroscope using iodine soln. in place of NaOH. After action is completed titrate with thio using starch. Cut of absorption top.

	New method	$\text{Cd}(\text{OAc})_2$ in NH_3	Br to BaSO_4	Gravi.
Mild steel	0.057	0.054	0.053	0.059

- 1919—SCHMITZ, FRIEDRICH. *Stahl u. Eisen*, Vol. 39, p. 406.
"Untersuchungen über die Gesetzmässigkeit der chemischen Einwirkungen der Gase auf Eisen und seine Verbindungen mit Nichtmetallen bei höheren Temperaturen."

Also in: *J. Soc. Chem. Ind.*, Vol. 38, p. 418.

Chem. Abstracts, Vol. 13, p. 3136 (1919).

Heats sample in hydrogen and oxygen to $1,100^\circ$ or

1,200°C. and recovers sulfur as H_2S or SO_2 to be measured as usual.

Results:

Heating in hydrogen at 1,200° C.

Material	S content	Evolved as H_2S
Cast iron	0.031	0.032 and 0.034
Tool steel	0.014	0.017 and 0.016
Wrought iron	0.043	0.046 and 0.046
High speed steel.....	0.026	0.027 and 0.028

Heating in oxygen.

Schulte's Method.

Pig iron	0.112	0.114 and 0.120
Cast iron	0.031	0.031 and 0.032
Cast steel	0.050	0.048 and 0.056
Cast steel	0.045	0.043 and 0.048

1920—CAMPBELL, E. D., AND SMITH, GEORGE F. *J. Ind. Eng. Chem.*, Vol. 12, p. 1020 (1920). "A Comparison of Accuracy in Analysis of Metallurgical Materials During the Past Twenty-five Years."

Chem. Abstracts, Vol. 14, p. 3607 (1920).

A very general review; figures compiled from Bureau of Standards averaged results of individual analysts. No obvious distinction between single results and averaged results.

Proposed limits for silicon and sulfur:

	Allowable difference	Probable limit of accuracy
Si	$\pm [0.005 + (0.02 \times \text{Si})]$	$\pm [0.002 + (0.003 \times \text{Si})]$
S	$\pm [0.003 + (0.03 \times \text{S})]$	$\pm [0.0005 + (0.005 \times \text{S})]$

Summarized results:

Number of standards		Range of cert. value	Mean cert. value	Allow diff. form applied to cert. value	Max. + and — from cert. value	
Cast Iron						
Si	11	1.267-2.64	1.93	±0.04	+0.05	—0.04
S	11	0.030-0.062	0.041	±0.004	+0.004	—0.004
Steel						
Si	35	0.003-0.303	0.120	±0.007	+0.03	—0.04
S	35	0.019-0.103	0.045	±0.004	+0.003	—0.003

DETERMINATION OF SULFUR IN IRON AND STEEL 155

Limit of accuracy of formula		Proportion of observers within lim. of accuracy	Per cent within lim. of accuracy
Cast Iron			
Si	± 0.008	42/111	38
S	± 0.001	70/162	43
Steel			
Si	± 0.002	154/369	42
S	± 0.001	244/485	50

INDEX

	PAGE
Abel, F. A.	59
Allen, A. H.	66
Analyses	
—samples	36-46
—screened sample	7
Antony, U.	113
Archbutt, L.	84
Arnold, J. O.	95
—and Hardy, H. J.....	78
—and Ibbotson	130
Auchy, G.	98-114-130
Aulich	110
Babbitt, H. C.	88
Bamber, H. K.	93
Bamber's method	15-25-26
Barium sulfate	
—analyses	19
—solubility	20-21
Bauer, O., and Classen, A. ..	71
—and Deiss	3-142-148
—and Heyn	3
Bayley, T.	71
Beckurts, H.	144
Bergmann	53
Berthier, M.	54
Berzelius	15-55
Bischoff, F.	118-119
Black	53
Blair, A. A.	18-103-150
—and Shimer, P. W....	2-117
Blanks	25-27-28-29-34
Blum, L.	85-90
Blount, B.	113
Bolling, R.	131
Booth, J. C., and Morfit, C....	56
Boucher, G. G.	99-104
Bourrey and Marquet	132
Boussingault	67
Brand, A.	71

	PAGE
Brandt, L.	143
Brearley, H., and Ibbotson, F.	119
Bromeis, C.	55
Brooks, H. E.	150
Brugman, W. F.	74
Bureau of Standards	
—precautions	18-23
—results	47
Cadmium sulfid	30-31
Camp, J. M.	85-143
Campbell, E. D., and Smith, G. F.	154
Campredon, L.	95-104
Carbon segregation	4
Carnot, A.	95
Carnot, A., and Goutal	105
Chance errors	50
Chloric acid method	14-27-28
Clark, W. W.	144
Classen	16-115
—and Bauer	71
Clymer, L. S.	46-88
Cohen, J. B.	84
Colorimetric end point	21
Constant errors	49
Craig, G.	70
Crobaugh, F. L.	91-110-124
Crystallization of metal	3
Deiss and Bauer	3-142
Dickson, W. E.	122
Distribution	
—of results	50-51-52
—of sulfur	3
Dougherty, G. T.	121-124
Drown, T. H.	67
Dudley, C. B.	106
Dussier, E.	130
Dust (sulfur)	26

	PAGE		PAGE
Eastwick, A. T.	89	Grinding (fine)	8
Edwards, C. A.	4	Gröndahl, V.	79
Eggertz, M. W.	61	Guenyveau	54
Eggertz, V.	58-75	Gurlt, A.	57
Elliott, A. H.	64	Hamilton, H. B.	62
Elliott, T. G.	141	Hardy, H. J., and Arnold, J. O.	78
Emmerton, F. A.	69	Hatfield, W. H.	4
Eng. Soc. West. Penna.	108	Hattensaur, G.	85
Equations for sulfur	31	Hees, J. K.	132
Errors		Helmar (and Noyes)	115
—chance	50	Herting, O.	106-110
—constant	49	Hibsch, J. E.	68
Evolution flask	17	Hillebrand, W. F.	138, 149
—method16-18-29-30-31		Hofman and Wanjukow	23
Fay, H.	18-150	Hooper, H. A.	91
Ferric oxide, colloidal	27	Howe, H. M.	4
Ferrous sulfid	2	Ibbotson, F., and Brearley, H.	119
Field, H. E.	122	Iodine end point	21-29
Fine grinding	8-9	Ireland, W. G.	123
Fischer, H.	144	Isham, H., and Aumer, J.	132
Flask (sulfur)	17-18	Jaboulay, E.	137
Föhr	76	Janoyer, M.	56
Forbes, D.	60	Jannasch and Richards	82
Ford, A. P., and Willey, O. G.	125	Johnson, C. M.	147
Forrestier, A.	96	Johnson, E. S.	106
Foulk, C. W.	99	Jornstorff, J. von	96
Franke, E.	109	Keeler, W. I.	141
Franklin, F. H.	145	Kinder, H.	132-139
Fresenius, C. R.	114	Kleine, A.	123-140
Fresenius, R.	67	Knight, S. S.	124
—and Hintz, E.	99	Koninck, L. L. de	63-80-96
Fricke, L.	126	—and Dietz	63
Friedheim, C.	126	Koppmayer, M.	66
Furman, H. Van F.	126	Krug, C.	126-143
Fusion methods	13	Kuster, F. W., and Thiel, A.	111
Giolitti, F., and Marcantonio, M.	141	Laister, C. P.	150
Gintl, M. W.	16-61	Laudis, E. K.	107
Gladding, T. S.	93-100	Ledebur, A.	113
Goldenberg, L. A.	151	Leeuwen, J.	90
Goutal and Carnot, A.	105		
Grant	147		

	PAGE		PAGE
Leutscher, J.	81	Nicholson, E. C., and Price, D. S.	57
Liberating sulfur	12	Nicklés, J.	59
Lindsay, W. G.	115	Nitric acid method	22-23
Lippert, G.	59	—solution	14
Lord, N. W.	123	Noad, H. M.	58
Lord and Demorest	18-146	Nostitz and Jankersdorf	130
Lucas, M.	100	Noyes, A. W., and Helmar ..	115
Lucion, M.	81	Olsen, J. C.	126
Lunge, G.	96	Orthey, M.	130-134-135-136
Lunge and Berl	139	Osann, B.	148
Macfarlane, W.	137	Osmond, M.	72
MacPherran, R. S.	125	Oxidation methods	14
Mackenzie, J. K.	91	Parry and Morgan	92
Mahlie, W. S.	152	Payne, H. L.	90
Manganese sulfid	2	Perillon	72
Marinot, A.	153	Peters, J.	73
Marsh, C. W.	83	Peters, S.	64
Matthewman, F. A.	101	Petrén, J.	127
McCabe, C. R.	127	Phillips, F. C.	96-101-148
McFarlane, J., and Gregory, A. W.	128	Phillips, H. J.	153
Meade, R. K.	107	Phosphorus segregation	4
Measuring sulfur	19	Piesse, C. H.	65-66
Meineke, C.	81-111	Pinsl, H.	151
Meineke, K.	16-63	Platz, B.	77-83
Methods for sulfur	10-11-33	Prechtl, J. J.	55
Methyl sulfid	18	Precision conditions	22-48
Meurice, A.	133	—of results	46
Miller, R., and Walters, H. E.	120	—of standardization	33
Millings	9	Preuss, G.	138-140-146
Mills, C. G.	137	Price, D. S., and Nicholson, E. C.	57
Misson, G.	147	Prost, E.	82-123
Möller, G.	75	Pulsifer, H. B.	127-149-151
Molyneaux, M.	153	Purification of barium sulfate 21-25	
Moore, M. J.	111	Raymond, E.	134
Morfit, C., and Booth, J. C...	56	Read, E. J.	97
Morgan, J. J.	76-79-101	Reinhardt, C.	73-84-128
Morgan and Parry	92	Reis, M. A. von.....	79-83-94
Morrell, T. T.	64	—and Wiggert, F.	86
Muller, E., and Diethelm, B.	139		
Naske, T.	117		
Neumann, B.	133		

	PAGE
Results	33-35-46
—precision of	46-47
—distribution of	50-1-2
Richards, T. W., and Parker, H. G.	97
—and Jannasch	82
Richters, E.	62
Riemer, A.	112
Rinman, L.	73
Ripper, M.	90
Rocholl, H.	71
Rollet, A.	69
Roos, J. O.	129
Rosenhain, W.	137
Rossi, A. J.	87
Roziers,	53
Rubber connections	16
Rüdisüle, A.	140
Samples analysed	35-46
Sampling	8-9
Sauveur, A.	4
Scheurer-Kestener	72
Schindler, W.	92
Schmidt, A.	138
Schmitz, F.	153
Schneider, A.	89
Schneider, L.	92
Schott, E. A.	138
Schulte, W.	102-107-129
Scott, W. W.	18-150
Segregations	3-4
Seyler, C. A.	123
Shimer and Blair	2-117
Siedener, C. F.	130
Silicon determination	46
Sleeper, J. F.	94
Sloane, T. O'C.	69
Sodium fluosilicate	28
Solidification of metal	3
Solubility of barium sulfate	19-20
—of sulfids	5-6-17
Spang	143
Sprenger	74

	PAGE
Spüller, J., and Kahlmann, S.	94
Standardization of solutions	31-32
Stehman, J. V. R.	121
Sulfur	
—flask	17-18
—liberation	12
—measuring	19
—prints	3-5-6-7-17
—segregation	4-5-6
Sulfids in materials	1-2-4
Szász, E.	137
T., J.	109
Tamm, A.	70-77
Thill, J.	112
Thill and Kuster	111
Thörner, W.	82-85-91
Tosh, E. G.	61
Trautman, W.	139
Treadwell-Hall	18-129
Troilius, M.	72
Vauquelin, C.	53
Vita, A., and Massenez, C.	143-147
Volatilization method	13
Vosmaer, A.	83
Wagner, R.	68
Walters, H. E., and Miller, R.	120
Wanjukow and Hofman	23
Wedding, H.	87
Wencelius, A.	122
Wennmann, D. A.	142
White, C. H.	18-149
Wilborgh, J.	75
Wiggert, F., and Reis, von... ..	86
Willey, O. G., and Ford, A. P.	125
Williams, F. H.	89
Williams, W. M.	65
Wilson, J. M.	88
Winder, B. W.	82
Wrightson, F. C.	55
Ziegler	70
Zschiegner, H.	149

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